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目　次

STUDIES ON BOUND WATER IN FISH MEAT MUSCLE (III)

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VI. ESTIMATION BY THE COBALTOUS CHLORIDE AND BY THE ELECTRICAL RESISTANCE METHODS OF THE AMOUNT OF BOUND WATER IN FISH MEAT IN VARIOUS CONDITIONS.

In this experiment, the amounts of Bound Water in raw fresh meat, dried meat, salted meat, fermented meat and decomposed meat of various kinds of fish were estimated by the cobaltous chloride method, and by the electrical resistance method.

1. Experimental methods.

(1) The method of estimating the amount of Bound Water.

The method chosen for estimating the amount of Bound Water was Oyagi's[12c]. The calculation was carried out by the same method as described in the earlier reported Exp. III. 1, (1), (II, B)[35a].

To calculate the amount of Bound Water (R. B.) in the samples (not dyed sample), the total amount of water (R. T.) in the like same sample of each material was determined by the usual drying method.

The calculating formula is as follows:

$$R.\ B. = \frac{(100 - R.\ T.)\ (W_1 - W_2)}{W_2} \quad \text{-------------} \quad (15)$$

where, W_1 is the weight at the point where the colour of the sample changes from pink to pure blue, or the apparent constant value of the weight of the sample during the drying at 30°C, W_2 is the constant weight of the sample during the drying at 110°C. The amount of Free Water (R. F.) in the sample, is calculated as follows:

$$R.\ F. = R.\ T. - R.\ B. \quad \text{----------------} \quad (16)$$

In this calculation, the amount of Bound Water per gm of the dried matter of the sample was supposed to remain unchanged during the steeping of the sample in the cobaltous chloride solution.

(2) The electrical resistance method.

The method for estimating by the electrical resistance was the same as in the previously described Experiment Ⅲ, 1, (1), (Ⅳ). The sample of fish meat filet (4×2×2 cm.) was impaled upon two copper poles (6.7 cm. in length and 0.17 mm. in diameter) fixed on the insulated bakelite plate at definite distance. The electrical resistance was made by Fuji Radio Co., its cycle was 50, and its type was Wheatstone's bridge. The estimating temperature of drying of fish meat was 19°C and 20°~25°C; the sample which was thrust through by the poles was placed in the desiccator before the estimation of electrical resistance. Thus the state of water in the sample was determined by the electrical resistance during the drying.

2. Experimental results and considerations.

(1) Determination of the amount of Bound Water by Oyagi's method.

The results on Sandfish (*Arctoscopus japonicus STEINDACHNER*), Squid (*Ommastrephes sloani pacificus*) and Flat-fish (*Kareius bicoloratus BASILEWSKY*) are shown in Table 24 and Fig. 33.

As stated earlier in Experiment Ⅲ. 1[38a], the sign B. P. in Table 24 and Fig. 33 is the point at which the colour of pieces of dyed fish meat steeped in the cobaltous chloride solution turns to pure blue from pink in the course of drying at 30°C. The amount of water estimated at point B. P. is represented as the amount of Bound Water. But as shown in the experiment there is another point, C. P., which is recognized as the apparent constant weight of water in the sample in the course of drying at 30°C from 1 to 3 hours after the appearance of the point B. P.

Discussing Bound Water from its binding strength, the amount of water determined by the cobaltous chloride method between the points B. P. and C. P. in the course of drying at 30°C, is regareded as the amount of Bound Water. The author calls the amount of water at point B.P. the maximum value of the amount of Bound Water, and the amount of water at point C. P. the minimum value of the amount of Bound Water. The values of the amount of Bound Water at those two points were estimated on the samples of various kinds of fish.

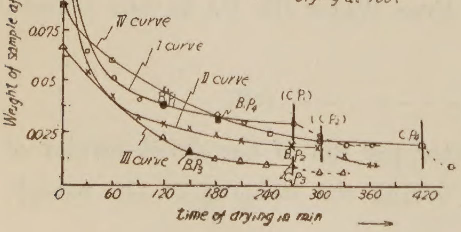


Fig.33 Variation in the amounts of water in the drying of several fish meats by the cobaltous chloride method. (Oyagi's method)

Table 24. Variation in the amounts of water in the drying of several fish meats by the cobaltous chloride method (Oyagi's method).

Drying time in min.	Sand fish meat: Change of the weight of sample (gm)	Sand fish meat: g※ (gm)	Sand fish meat: Drying temp. (°C)	Squid fish meat: Change of the weight of sample (gm)	Squid fish meat: g※ (gm)	Squid fish meat: Drying temp. (°C)	Flat fish meat: Change of the weight of sample (gm)	Flat fish meat: g※ (gm)	Flat fish meat: Drying temp. (°C)
0	0.1352	10.76	25°~30°C	0.0641	5.04	25°~30°C	0.0883	3.57	15°~20°C
30	0.0534	3.63		—	—			—	
60	0.0418	2.63		—			0.0613	2.17	
90	0.0319	1.77		—	—		—	—	
120	0.0282	1.39		0.0242	1.28		0.0476	1.46	
150	0.0265	1.30		0.0173	0.63 ($B.P_3$)		—	—	
180	0.0242	1.10		0.0138	0.30		0.0331	0.72 ($B.P_4$)	
210	0.0220	0.91 ($B.P_2$)		0.0130	0.226		—	—	
240	—	—		0.0120	0.132		0.0253	0.31	
270	0.0196	0.70		0.0120	0.132 ($C.P_3$)		-	-	
300	0.0195	0.69 ($C.P_2$)		—	—	100° ~ 105°C	0.0231	0.198	
330	0.0157	0.36	100° ~ 105°C	0.0106	0.00		—	—	
360	0.0115	0.00		0.0106	0.00		0.0228	0.180 ($C.P_4$)	
370	0.0115	0.00					—	—	
420							0.0228	0.180	
480							0.0195	0.010	100° ~ 105°C
540							0.0193	0.00	
600							0.0193	0.00	
Remarks	See II curve in Fig. 33			See III curve in Fig. 33			See IV curve in Fig. 33		

Note : I curve in Fig. 33 is the same curve as shown in Fig. 7. previous Experiment III, 1.
※ Gm of water per gm of bone dried sample.

(I) Determination of the amount of Bound Water by the cobaltous chloride method on the raw fresh meat of various kinds of fish.

The results derived from using Oyagi's method on the raw fresh meat of Squids (*Ommastrephes sloani pacificus* and *Loligo bleekeri KEFERSTEIN*), Flat-fishes (*Microstomus achve JORDAN et STARKE, Atheresthes evermanni JORDAN et STARKE, Kareius bicoloratus BASILEWSKY, Limanda herzensteini JORDAN et SNYDER* and *Paralichthys olivaceus TEMMINCK et SCHLEGEL*), Herring (*Clupea harengus SINNEUS*), Sardine (*Engraulis japonicus TEMMINCK et SCHLEGEL*), Mackerel (*Scomber japonicus HOUTTUYN*),

Atka Mackerel (*Pleurogrammus azonus JORDAN et METZ*), Horse Mackerel (*Trachurus japonicus TEMMINCK et SCHLEGEL*), Sand fish (*Arctoscopus japonicus STEINDACHNER*) and Globe-fish (*Sphaeroides rubripes TEMMINCK et SCHLEGEL*) are shown in Tables 25, 26 and 27. Table 25 shows the minimum values of the amount of Bound Water in the samples; Table 26 shows the maximum values of the amount of Bound Water; Table 27 shows the averages of those values of the amount of Bound Water per 100 gm of the dried matter of the samples.

From Tabler 25, 26 and 27 it is clear that the minimum amount of Bound Water is 10—48 gm (25.2 gm on the average) per 100 gm of the dried matter of the fresh meat, and the maximum amount of Bound Water is 55—82 gm (63.2 gm on the average). Supposing that Free Water has evaporated first when the raw fresh fish meat is dried, the total amount of water remaining in the fish meat is considered to be Bound Water at the time when the water-content of the meat shows about 20% (the minimum water-content) or 40% (the maximum water-content).

Table 25. Minimum values of the amount of Bound Water in the raw fresh meat of various kinds of fish.

Samples \ Water Contents	Total Water (R. T. %)	Free Water (R. F. %)	Bound Water (R. B. %)	$\frac{R.F.}{R.T.} \times 100$ (%)	$\frac{R.B.}{R.T.} \times 100$ (%)	g. (gm of Bound Water per gm of dried matter)	$\frac{g}{g+D.M} \times 100$ (%) (D.M = Dried matter)
Squid (*Ommastrephes sloani pacificus*)	(1) 83.51 (2) 81.64	81.43 80.64	2.18 3.48	97.50 95.85	2.50 4.15	0.132 0.220	11.6 18 0
Squid (*Loligo bleekeri KEFERSTEIN*)	79.89	70.26	9.60	88.00	12.00	0.477	32.3
Flat fish (*Microstomus achve JORDAN et STARKE*	76.18	72.50	3.68	95.16	4.84	0.154	13.3
Flat fish (*Atheresthes evermanni JORDAN et STARKE*	80.99	79.28	1.71	97.87	2.13	0.09	8.25
Flat fish (*Kareius bicoloratus BASILEWSKY*	(1) 79.19 (2) 78.64	74.51 74.39	4.66 4.25	94.11 94.59	5.89 5.41	0.224 0.199	18.3 16.6
Flat fish (*Paralichthys olivaceus TEMMINCK et SCHLEGEL*)	78.02	73.30	4.72	93.90	6.10	0.215	17.7
Herring (*Clupea herengus SINNEUS*)	(1) 81.64 (2) 80.62	78.84 76.70	2.80 3.92	96.50 95.13	3.44 4.87	0.152 0.202	13.1 16.6
Sardine (*Engraulis japonicus TEMMINCK et SCHLEGEL*)	(1) 76.55 (2) 79.34	71.80 74.54	4.37 4.80	93.80 94.00	6.20 6.00	0.202 0.232	16.6 18.8
Sand fish (*Arctoscopus japonicus STEINDACHNER*)	80.30	73.30	7.00	91.28	8.72	0.356	26.2
Atka Mackerel (*Pleurogrammus azonas JORDAN et METZ*)	(1) 80.00 (2) 83.95 (3) 80.99	71.26 80.47 79.28	8.74 3.48 1.71	89.09 95.85 97.87	10.93 4.15 2.13	0.437 0.216 0.09	30.4 17.8 8.25

Table 26. Maximum values of the amount of Bound Water in the raw fresh meat of various kinds of fish.

Samples \ Water Contents	Total Water (R.T. %)	Free Water (R.F. %)	Bound Water (R.B. %)	$\frac{R.F.}{R.T.}\times 100$ (%)	$\frac{R.B.}{R.T.}\times 100$ (%)	g. (gm of Bound Water per gm of dried matter)	$\frac{g}{g+D.M}\times 100$ (%) (D.M = Dried matter)
Squid (*Loligo bleekeri* KEFERSTEIN)	(1) 76.27	59.03	17.24	77.3	22.7	0.726	42.0
	(2) 78.19	60.85	17.34	77.8	22.2	0.778	43.8
	(3) 78.73	59.56	19.17	75.6	24.4	0.896	47.2
	(4) 78.45	60.21	18.24	76.7	23.3	0.845	45.8
Squid (*Ommastrephes sloani pacificus*)	76.62	63.58	13.04	82.9	17.1	0.557	35.8
Sardine (*Engraulis japonicus* TEMMINCK et SCHLEGEL	(1) 76.70	65.66	11.04	85.6	14.4	0.474	32.1
	(2) 76.70	59.50	17.20	77.5	22.5	0.738	42.5
Sand fish (*Arctoscopus japonicus* STEINDACHNER)	(1) 80.51	67.40	13.11	83.7	16.3	0.673	40.2
	(2) 80.51	66.79	13.72	82.9	17.1	0.704	41.3
Horse Mackerel (*Trachurus japonicus* TEMMINCK et SCHLEGEL)	(1) 76.14	57.60	18.54	75.7	24.3	0.777	43.7
	(2) 73.20	54.28	18.92	74.1	25.9	0.706	41.4
Globe fish (*Sphaeroides rubripes* TEMMINCK et SCHLEGEL)	(1) 80.07	68.97	11.10	86.1	13.9	0.557	35.8
	(2) 80.10	65.40	14.67	81.0	19.0	0.736	42.4
Flat fish (*Limanda herzensteini* JORDAN et SNYDFR)	(1) 78.88	52.96	25.92	67.1	32.9	1.230	55.2
	(2) 78.74	54.99	23.75	69.8	30.2	1.117	52.8
Mackerel (*Scomber japonicus* HOUTTUYN.	76.62	63.58	13.04	82.9	17.1	0.557	35.8

Table 27. Amount of Bound Water in the raw fresh meat of various kinds of fish.

Samples \ Amount of Bound Water	Minimum amount of Bound Water	Maximum amount of Bound Water	Samples \ Amount of Bound Water	Minimum amount of Bound Water	Maximum amount of Bound Water
Squid (*Ommastrephes sloani pacificus*)	17.5	55.7	Flat fish (*Paralichthys olivaceus* TEMMINCK et SCHLEGEL)	21.5	—
Squid (*Loligo bleekeri* KEFERSTEIN)	47.7	81.1	Flat fish (*Limanda herzensteini* JORDAN et SNYDER)	—	54
Sardine (*Engraulis japonicus* TEMMINCK et SCHLEGEL)	21.7	60.6	Atka Mackerel (*Pleurogrammus azonas* JORDAN et METZ)	37.1	—
Sand fish (*Arctoscopus japonicus* STEINDACHNER)	35.6	68.8	Mackerel (*Scomber japonicus* HOUTTUYN)	—	55.7
Flat fish (*Kareius bicoloratus* BASILEWSKY	21.1	—	Horse Mackerel (*Trachurus japonicus* TEMMINCK et SCHLEGEL)	—	64.8
Flat fish (*Microstomus achve* JORDAN et STARKE)	15.4	—	Globe-fish (*Sphaaroides rubripes* TEMMINCK et SCHLEGEL)	—	64.6
Flat fish (*Atheresthes evermanni* JORDAN et STARKE)	9.0	—	Range (Average)	10～48 (25.2)	55～80 (63.2)

However, at the time of the evaporation of water from the meat, the mechanism of water evaporation varies practically somewhat with the differences in conditions between the inner and surface parts of the meat. That is to say, at the surface because of excess drying, the amount of Bound Water decreases and some amount of Free Water rests in the meat.

Here, it is noteworthy that the amount of Bound Water in the fish meat is not necessarily always the same, because the amount of Bound Water varies apparently with the kind of fish. Even in the same kind of fish, the amount of Bound Water is recognized to vary with each body. Beside those factors, the amount of Bound Water is supposed to vary with catching season in keeping with the chemical components and properties of the fish meat, such as the water-content and protein and fat.

Higuchi[23] has estimated the amount of Bound Water in Squid and Flat-fish meat by a method concerning the depression of the freezing point and calorimetric method. The present author has calculated Higuchi's results as follows: the amount of Bound Water in Squid is 13.4 gm per 100 gm of the dried matter of the sample, and 18.7 gm for Flat fish meat. These values are in correspondence with the minimum values estimated by the cobaltous chloride method. As described in Experiment Ⅲ, 1, (2), (Ⅱ), B, the minimum value of the amount of Bound Water is recognized to be the Colloidal Bound Water, and the maximum amount of Bound Water is considered to be the Biological Bound Water.※

(Ⅱ) The amount of Bound Water estimated in the dried meat of several kinds of fish by the cobaltous chloride method.

The maximum and minimum values of the amount of Bound Water of Squid (*Ommastrephes sloani pacificus* and *Loligo bleekeri KEFERSTEIN*), Mackerel (*Scomber japonicus HOUTTUYN*), Atka Mackerel (*Pleurogrammus azonus JORDAN et METZ*), Sand-fish (*Arctoscopus japonicus STEINDACHNER*), Globe-fish (*Sphaeroides rubripes TEMMINCK et SCHLEGEL*), Sardine (*Engraulis japonicus TEMMINCK et SCHLEGEL*) and Flat fish (*Limanda herzensteini JORDAN et SNYDER*) by the cobaltous chloride method are shown in Tables 28 and 29.

Fig. 34 shows the relation between the total amount of water of each sample of various kinds of fish meat and the amount of Free Water, or the relation between the maximum and the minimum values of Bound Water of each sample. Fig. 35 shows the amount of Bound Water per gm of the dried matter of each sample in relation to the total amount of water in each sample. The curves in

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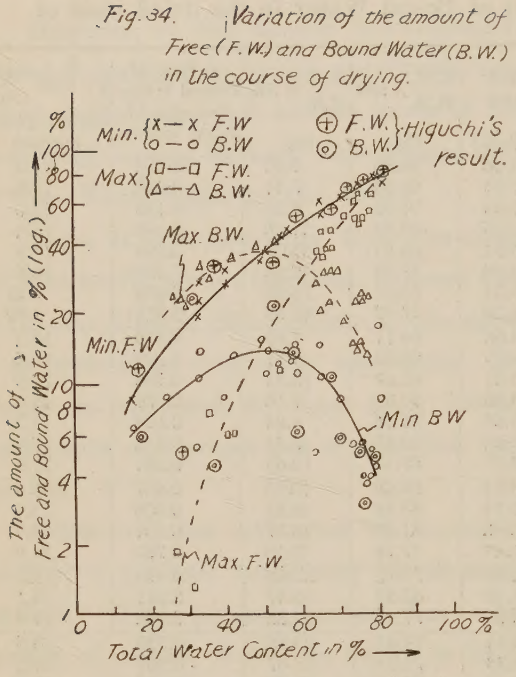
※The Biological Bound Water will be discussed in detail in further experiments.

Table 28. Minimum values of the amount of Bound Water in the dried meat of various kinds of fish.

Samples and Treatments \ Water Contents	Total Water (R. T. %)	Free Water (R. F. %)	Bound Water (R. B. %)	$\frac{R.F.}{R.T.} \times 100$ (%)	$\frac{R.B.}{R.T.} \times 100$ (%)	g. (gm of Bound Water per gm of dried matter)	$\frac{g}{g+D.M} \times 100$ (%) (D.M = Dried matter)
Squid (*Ommastrephes sloani pacificus*) (Sun-drying)	(1) 77.33	73.33	4.00	94.80	5.20	0.176	15.0
	(2) 74.64	69.11	5.53	92.59	7.41	0.218	17.9
	(3) 62.87	57.83	5.04	91.98	8.02	0.136	12.0
	(4) 38.53	26.48	12.05	68.72	31.28	0.196	16.4
	(5) 31.80	21.28	10.52	66.91	33.09	0.154	13.3
	(6) 31.74	18.10	13.64	57.02	42.98	0.199	16.6
	(7) 31.44	26.10	5.34	83.01	16.99	0.078	7.25
	(8) 14.58	8.38	6.20	57.47	42.53	0.073	6.82
Atka Mackerel (*Pleurogrammus azonas JORDAN et METZ*) (Half-dried)	(1) 79.17	74.51	4.66	94.11	5.89	0.224	18.3
	(2) 78.64	74.39	4.25	94.59	5.41	0.199	16.6
	(3) 77.51	69.50	5.01	86.67	10.33	0.356	27.0
	(4) 77.33	73.33	4.00	94.82	5.18	0.176	15.0
	(5) 76.18	72.50	3.68	95.16	4.84	0.154	13.3
	(6) 74.64	69.11	5.54	92.59	7.41	0.218	17.9
	(7) 69.00	60.29	8.71	87.37	12.63	0.281	21.9
Ditto (Sun-drying)	(1) 80.00	71.26	8.74	89.09	10.93	0.437	30.4
	(2) 64.90	54.16	10.74	83.45	16.55	0.306	23.4
	(3) 57.90	46.92	10.98	81.03	18.97	0.261	19.9
	(4) 55.90	43.47	12.43	77.76	22.24	0.282	21.9
Ditto (Drying by heating)	(1) 63.20	68.74	14.46	77.12	22.88	0.393	28.2
	(2) 40.50	27.35	13.15	67.53	32.47	0.221	18.1
	(3) 38.30	29.54	8.76	77.12	22.88	0.142	12.4
Ditto (Salting and Drying)	(1) 57.00	42.43	14.44	74.44	25.56	0.339	25.3
	(2) 55.00	41.64	13.33	72.33	27.67	0.269	21.2
	(3) 52.90	40.80	12.10	77.12	22.88	0.257	20.4
	(4) 49.30	35.66	13.64	72.33	27.67	0.269	21.2
	(5) 48.60	37.65	10.95	74.73	25.27	0.213	17.5
	(6) 47.60	32.99	15.51	67.41	32.59	0.296	22.9

Table 29. Maximum values of the amount of Bound Water in the dried meat of various kinds of fish.

Samples and Treatments \ Water Centents	Total Water (R. T. %)	Free Water (R. F. %)	Bound Water (R. B. %)	$\frac{R.F.}{R.T.} \times 100$ (%)	$\frac{R.B.}{R.T.} \times 100$ (%)	g. (gm of Bound Water per gm of dried matter)	$\frac{g}{g+D.M} \times 100$ (%) (D.M = Dried matter)
Squid (*Loligo bleekeri KEFERSTEIN*) (Sun-drying)	(1) 34.31	7.38	26.93	21.50	78.50	0.410	29.0
	(2) 26.42	1.84	24.58	6.96	93.04	0.334	25.0
	(3) 25.61	0.76	28.85	2.97	97.03	0.334	25.0
Mackerel (*Scomber japonicus HOUTTUYN*) (Half-dried)	(1) 73.27	50.68	22.59	68.20	30.80	0.845	45.7
	(2) 73.38	50.21	23.17	68.40	31.60	0.873	46.6
	(3) 73.49	49.74	23.75	67.70	32.30	0.896	47.2
	(4) 64.95	43.75	21.20	67.30	32.70	0.605	37.8
Sandfish (*Arctoscopus japonicus STEINDACHNER*) (Sun-drying)	(1) 52.71	11.76	40.95	22.30	77.30	0.862	46.2
	(2) 28.57	5.15	23.42	18.02	81.98	0.328	24.7
Globe-fish (*Sphaeroides rubripes TEMMINCK et SCHLEGEL*) (Sun-drying)	(1) 39.47	5.82	33.65	14.70	85.30	0.556	35.7
	(2) 39.47	5.94	33.53	15.00	85.00	0.554	35.6
Squid (*Ommastrephes sloani pacificus*) (Half-dried)	(1) 74.10	60.17	13.93	81.20	18.80	0.538	35.0
	(2) 73.50	58.93	14.57	80.10	19.90	0.550	35.4
	(3) 73.80	59.55	14.25	80.70	19.30	0.544	35.2
	(4) 70.10	51.26	18.84	73.10	26.90	0.603	37.6
	(5) 63.26	35.38	27.88	55.90	44.10	0.759	43.1
	(6) 66.68	43.99	22.64	65.90	34.10	0.681	40.5
Flat fish (*Limanda herzensteini JORDAN et SNYDER*) (Half-dried)	(1) 76.61	53.06	23.55	69.20	30.80	1.007	50.3
	(2) 68.55	37.98	30.57	55.40	44.60	0.972	49.3
	(3) 65.21	34.98	30.23	53.64	46.34	0.864	46.3
	(4) 66.88	36.80	30.50	54.39	45.61	0.921	47.9
Sardine (*Engraulis japonicus TEMMINCK et SCHLEGEL*) (Sun-drying)	31.76	1.26	30.50	3.96	96.04	0.447	30.9



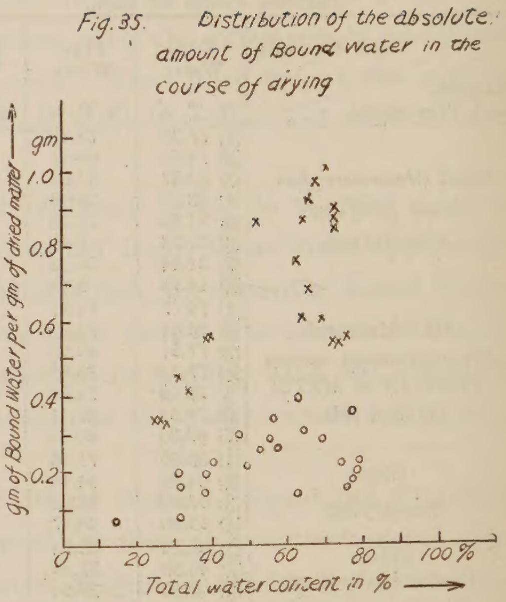


Fig. 34 are formed by joining the massed points for the amounts of Free Water and Bound Water (the maximum and the minimum values) of all the samples. These curves are considered to show the variation of the amounts of Free and Bound Water during the drying of fish meat.

From Fig. 34 it is clear that with the drying, the percentage of the amount of Free Water decreases and the percentage of the amount of Bound Water increases relatively; the relative amount of Bound Water for total amount of Water shows the maximum value at about 40∼50% of the total amount of water in the fish meat. With further dehydration, the percentage of the amount of Bound Water decreases. When the maximum value of the amount of Bound Water is determined, the percentage of the amount of Bount Water for the total amount of Water in the fish meat is from about 25% (minimum) to 75% (maximum) as seen in Table 28 and 29.

Higuchi's results for Squid and Flat fish meat during the drying which were together shown in Fig. 34 agreed generally with the minimum value of the amount of Bound Water (Colloidal Bound Water) obtained by the present author. It is interesting that the values of the amount of Bound Water obtained by the thermodynamic methods such as the one concerning the depression of the freezing point and the calorimetric method by Higuchi agreed almost with the results obtained by the chemical methods such as the cobaltous chloride which is different

from the thermodynamic methods in the idea of the determination. This agreement encourages the present author to believe that the minimum value of the amount of Bound Water obtained by the cobaltous chloride method (the amount of water at the point of C. P. in the course of drying of the sample) should be considered as the Colloidal Bound Water. This conclusion has also been substantiated by the previously reported Experiment Ⅲ, 1.

From Fig. 35 the absolute value of the amount of Bound Water per gm of the dried matter of the fish meat apparently decreases generally with the drying of the sample.

(Ⅲ) Results obtained by the cobaltous chloride method on the salted fish meat.

Tables 30 and 31 show the amounts of Bound Water in the salted fish meat —Atka Mackerel (*Pleurogrammus azonus JORDAN et METZ*), Squid (*Loligo bleekeri KEFERSTEIN*) and Mackerel (*Scomber japonicus HOUTTUYN*).

Salted Atka Mackerel meat was prepared by the dry-salting and brine-salting processes. Salted Mackerel and Squid were made by dry-salting process. The amount of salt used was 20% by weight of the raw material in the dry-salting process.

The brine was saturated salt solution. The amounts of Bound Water in these salted fishes were determined by the cobaltous chloride method (Oyagi's).

Fig. 36 shows the variation of the amount of Bound Water in the salted Atka Mackerel, Squid and Mackerel meat at certain intervals after the salting.

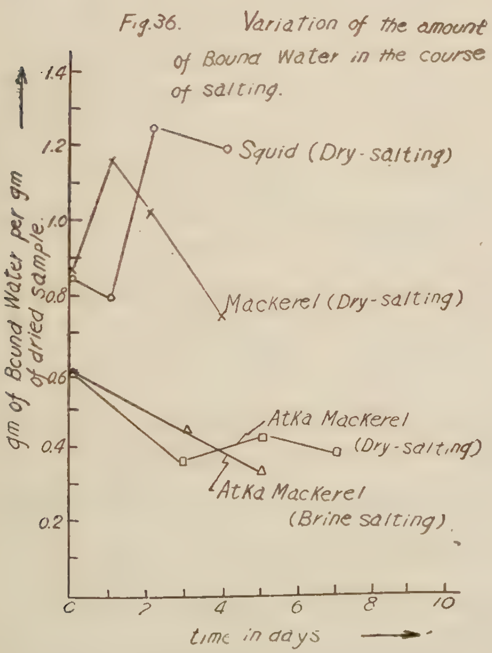


Fig. 36. Variation of the amount of Bound Water in the course of salting.

Table 30 shows the variation of the amount of Colloidal Bound Water (the minimum value of the amount of Bound Water at C. P.) in Atka Mackerel meat at certain intervals after the salting process. Table 31 shows the variation of the amount of Biological Bound Water (the maximum values at B. P.) in Mackerel and Squid meat at intervals after the salting process.

From Tables 30 and 31, it is observed that the total amount of water decreases with the lapse of hours after the salting process because of the osmotic dehydration

Table 30. Variation in the amount of Colloidal Bound Water in Atka Mackerel meat at certain intervals after salting.

Samples, Treatments and Days \ Water Contents		Total Water (R. T. %)	Free Water (R. F. %)	Bound Water (R. B. %)	$\frac{R.B.}{R.T.} \times 100$ (%)	$\frac{R.F.}{R.T.} \times 100$ (%)	g (gm of Bound Water per gm of dried matter)
Atka Mackerel (*Arctoscopus japonicus* *STEINDACHNER*) (Brine-salting)	Raw fish meat	80.5	68.92	11.58	14.39	85.61	0.594
	3 days after	61.7	44.73	16.97	27.53	72.47	0.443
	5 〃 〃	62.8	50.52	12.28	19.56	80.44	0.330
	7 〃 〃	63.1	—	—	—	—	—
Ditto (Dry-salting)	Raw fish meat	80.5	68.92	11.58	14.39	85.61	0.594
	3 days after	61.1	47.18	13.92	22.88	77.12	0.358
	5 〃 〃	59.7	42.62	17.08	28.60	71.40	0.425
	7 〃 〃	42.4	20.80	21.60	59.95	49.50	0.375

Table 31. Variation in the amount of Biological Bound Water in Squid and Mackerel meat at certain intervals after salting.

Samples, Treatments and Days \ Water Contents		Total Water (R. T. %)	Free Water (R. F. %)	Bound Water (R. B. %)	$\frac{R.B.}{R.T.} \times 100$ (%)	$\frac{R.F.}{R.T.} \times 100$ (%)	g (gm of Bound Water per gm of dried matter)
Squid (*Loligo bleekeri* *KEFERSTEIN*) (Dry-salting)	Raw fish meat	78.45	60.21	18.24	23.26	76.74	0.845
	1 day after	62.52	33.73	29.79	46.05	53.95	0.795
	2 days 〃	61.94	14.41	47.53	76.74	23.26	1.249
	4 〃 〃	60.44	13.24	47.20	78.10	21.90	1.193
Mackerel (*Scomber japonicus TEMMINCK et SCHLEGEL*) (Dry-salting)	Raw fish meat	73.38	50.21	23.17	31.58	68.42	0.873
	1 day after	58.04	9.62	48.42	83.43	16.57	1.154
	2 days 〃	55.65	10.32	45.33	81.46	18.54	1.022
	4 〃 〃	57.94	26.68	31.30	53.99	46.01	0.745

by salt. The dehydrating action of the dry-salting process is greater than that of the brine-salting process. This fact agrees with the previous results of many investigators.[46]

In salted fish meat, the amount of Free Water decreases and the amount of Bound Water increases relatively. This fact agrees with the case of the dried fish meat.

However, the absolute amount of Bound Water in the Atka Mackerel meat per gm of the dried matter decreased somewhat with the lapse of days after the salting, as shown in Fig 36.

This fact is clearly due to the decomposition of fish meat protein, that is, to the denaturation of the protein by the salting.

In the case of Squid and Mackerel meat the increase in the absolute amount of Bound Water is not so clear as in Atka Mackerel as shown in Fig. 36.

(Ⅶ) The results of estimations of the amount of Bound Water in fermented fish meat and decomposed fish meat by the cobaltous chloride method.

(A) The variation of the amount of Bound Water in Soused Squid meat ("Shiokara" in Japanese) during its ripening.

The variation of the amount of Bound Water in Soused Squid meat was observed as follows:

Soused Squid meat ("Shiokara") is a Japanese special product which is made from cut Squid meat, its liver, and salt (sodium chloride). The author has prepared it by the following process. The body of fresh Squid (average weight of a Squid is 284 gm) was cut in small rectangular pieces (0 5 × 3 cm), and was mixed with NaCl and Squid liver, then was stirred every day for 4 weeks. The percentage of added NaCl was 15% of the weight of the cut Squid meat. The percentage of Squid liver added was 3% (A), and 6% (B), respectively by weight, of the cut Squid meat.

The amount of Bound Water in the Soused Squid meat was estimated by the cobaltous chloride method (Oyagi's method) after washing the surface of the cut Squid meat and adsorbed water attached to the surface of the meat.

Table 32. Variation in the minimum amount of Bound Water during the ripening of Soused Squid ("Shiokara")

(A) Squid liver added in 3%

Days of processing	Total Water (R. T. %)	Free Water (R. F. %)	Bound Water (R. B. %)	$\frac{R.F.}{T.R.} \times 100(\%)$	$\frac{R.B.}{R.T.} \times 100(\%)$	g. (gm of Bound Water per gm of dried matter)
0	82.63	79.38	3.25	96.06	3.94	0.187
4	85.66	82.95	2.71	96.83	3.14	0.189
7	89.00	87.38	1.62	98.17	1.83	0.147
10	82.44	82.01	0.43	99.47	0.53	0.024
21	87.46	87.22	0.24	99.72	0.28	0.019

(B) Squid liver added in 6%

Days of processing	Total Water (R. T. %)	Free Water (R. F. %)	Bound Water (R. B. %)	$\frac{R.F.}{T.R.} \times 100(\%)$	$\frac{R.B.}{R.T.} \times 100(\%)$	g. (gm of Bound Water per gm of dried matter)
0	82.63	79.38	3.25	96.06	3.94	0.187
4	88.54	85.84	2.70	96.95	3.05	0.232
7	89.03	86.63	2.40	97.30	2.70	0.219
10	81.15	80.09	1.06	98.69	1.31	0.056
21	82.17	82.20	0.97	98.81	1.19	0.054

The variation of the amount of Bound Water during the ripening of Soused Squid ("Shiokara") is shown as (A) and (B) in Table 32. The values there tabulated are the minimum amounts of Bound Water (the values of the amount of Bound Water at C. P.)

From Table 32 (A), (B), it is observed that the total amount of water increased gradually with the decomposition of fish meat protein by enzymatic action for the

first 10 days, and then the total amount of water decreased as a manifestation of the effect of dehydrating action. In the total amount of water, the amount of Free Water increased gradually and the amount of Bound Water decreased. This fact is contrary to the results obtained with the dried fish meat or the salted fish meat. The amount of Bound Water per gm of the dried matter of the fermented fish meat decreased during the ripening. But the amount of Bound Water was observed to increase contrarily during the incipient ripening of fish meat. This fact will be understood that the dried matter of fish meat decreases owing to the decomposition of fish meat protein, but the amount of Bound Water is hardly influenced. However, this conclusion is somewhat doubtful because of the supposition that the amount of Bound Water did not vary during the steeping of the sample in cobaltous chloride solution. It is certain that the variation of the amount of Bound Water in the fermented Squid meat is different from that in either the dried fish meat or the salted fish meat.

(B) The variation of the amount of Bound Water in the decomposed Atka Mackerel meat.

The variation of the amount of Bound Water in half dried Atka Mackerel meat (water-content 69%) which was left to the time of detecting tainted odour in the Petri dish at 30°C, was observed. The experimental results are shown in Table 33.

Table 33. Variation in the minimum amount of Bound Water in putrefied Atka Mackerel meat.

Days of processing	Total Water (R. T. %)	Free Water (R. F. %)	Bound Water (R. B. %)	$\frac{R.F.}{R.T.} \times 100(\%)$	$\frac{R.B.}{R.T.} \times 100(\%)$	g. (gm of Bound Water per gm of dried matter)
0	69.0	60.29	8.71	87.37	12.63	0.281
2	69.4	62.24	7.16	89.68	10.32	0.237
6	74.2	67.39	6.81	90.82	9.18	0.264

As shown in Table 33, the muscle tissue of fish meat decomposed with the putrefaction, the total amount of water increased gradually, and the tainted odour was notable already a day after the handling. It was observed that the amount of Free Water increased and the amount of Bound Water decreased with the putrefaction of fish meat. That is to say, the variation of the amount of Bound Water in the putrefied fish meat is similar to that in the fermented Squid meat. However, the variation of the absolute amount of Bound Water per gm of the dried matter of the sample is not clear.

In this experiment employing the cobaltous chloride method, the estimation

was very difficult owing to the softening of fish meat; estimation was made again by the electrical resistance measurement. The vapour tension method was also tried for estimating the amount of Bound Water in the putrefied fish meat, but this method was not satisfactory, because the volatile basic matters grew from the meat.

(2) Results of estimations by the electrical resistance of some fish meat.

Ueda, Ito and Nishi[47a] and Tamura[47b] have observed the variation of the electrical resistance in the carp meat fresh after the death. They stated that the electrical resistance decreased rapidly after a definite time after the death, and the lower the temperature is, the longer the time needed to decrese electrical resistance. The cause of the decreasing of electrical resistance is perhaps the change of the muscle tissue of fish meat by autolysis and bacterial action. Yamamura[47c] has observed that the specific electrical resistance of the direct current is 2,400～3,000 Ohms and of the alternating current of 1,000 cycles is 80～90 Ohms for the raw fresh meat of Horse Mackerel (*Trachurus japonicus TEMMINCK et SCHLEGEL*), Mackerel (*Scomber japonicus HOUTTUYN*) or Flat fish (*Limanda herzensteini JORDAN et SNYDER*). Tamura, Miyazaki and Kajiyama[47d] have studied the relation between the amount of penetrated NaCl in fish meat and the electrical resistance in the salted fish meat. Callow[47e] has also studied the distribution of the electrical resistance of the muscular tissue of farm-killed pigs and of pigs killed in factory or abattoir. Recently Yamada and Kitano[47f] have studied the variation of the electrical resistance and of pH value of the denatured myosin added with NaCl. Ito, Kyozuka and Sugizaki[47g] have also studied the electrical resistance of raw fresh fish meat, heated fish meat and chilled fish meat.

The present author has studied in his Experiment Ⅲ, 1, the variation of the electrical resistance of 50 cycles in samples of gelatine and fish meat having various water-contents, and has obtained the following results: the electrical resistance decreased somowhat with the decreasing of water-content at first, but it decreased gradually at points above a definite concentration or dryness, and thereafter it increased rapidly. The gradual increasing of the electrical resistance in the first stage was considered to be due to the increasing of the amount of Bound Water in inverse proportion to the decreasing of the Free Water. The rapid increasing in the next stage was considered to be due to the remaining of Bound Water which has strong force at the time when the amount of Bound Water which has weak binding force, decreased.

The amount of water estimated at the point of rapid increasing of the

electrical resistance was considered to be Colloidal Bound Water as compared with the results obtained by the cobaltous chloride and vapour tension methods.

Here, the author reports the results obtained by estimating the electrical resistance for some fish meat.

(I) Preliminary experiment

(A) Relation between the electrical resistance (50 cycles) and the distance of electrodes for various kinds of fish meat.

Table 34 and Fig. 37 show the relation between the electrical resistance of

Table 34. Relation between the electrical resistance of 50 cycles and the distance of the electrodes for various kinds of fish meat.

Samples / Distance of Electrodes	Whole body of a species of Surf-smelt	Fresh raw Atka Mackerel meat	Chilled Atka Mackerel meat	Salted Atka Mackerel meat	Unfresh raw Atka Mackerel meat	Freh raw Squid (*Loligo bleekeri*) meat
1.5cm.	0.395KΩ	0.266	—	—	0.162	0.77
2.0	0.400	—	—	0.030	0.178	1.11
2.5	0.530	0.363	—	—	—	1.25
3.0	—	—	0.063	0.040	0.194	—
3.5	—	—	—	0.048	0.228	1.45
4.0	—	0.455		—	—	—
4.7	—	—	—	—	0.268	2.0
5.0	0.655	0.540	—	0.050	—	—
5.4	—	—	0.075	—	0.298	—
6.0	0.780	0.576	—	0.060	0.305	—
6.9	—	0.700	—	—	0.332	—
8.0	—	0.735	0.083	—	0.378	—
9.0	—	0.870	—	—	0.453	—
10.0	—	0.950	0.105	—	0.485	—
Remarks	Water Content 75.8%			Total Water 70.2% NaCl 15.7%		

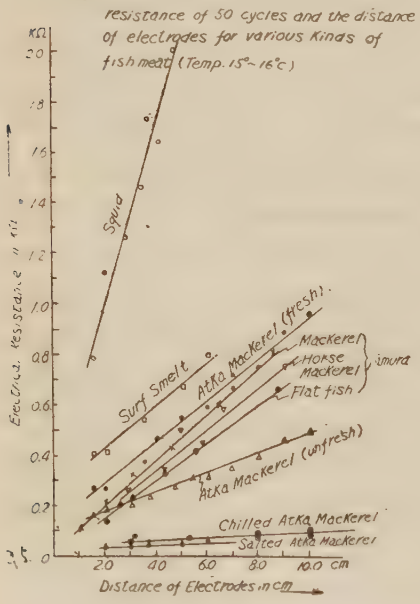


Fig 37. Relation between the electrical resistance of 50 cycles and the distance of electrodes for various kinds of fish meat (Temp. 15°~16°c)

50 cycles and the distance of the electrodes for various kinds of fish meat. In Fig. 37, the results obtained by Yamamura[47c] are written together. It was observed that the electrical resistance was proportional to the distance of electrodes and showed liner function. This result is the same as in the result obtained by Yamamura.

The electrical resistance of unfresh raw or chilled Atka Mackerel meat is less than that of fresh raw Atka Mackerel meat. This result agrees with the results obtained by Tamura[4b]. In salted Atka Mackerel meat, the electrical resistance decreased with the penetration of the electrolyte (NaCl).

(B) The electrical resistance of fish meat gruel.

According to the method employed by Tamura[47b], the present author ground 100 gm of raw fresh meat of Atka Mackerel and filtered it through gauze. This filtered meat was added with 200 c.c. of distilled water and made into fish meat gruel. It was separated in two parts: (A) Antisepticized gruel by toluene. (B) Non-antisepticized gruel. The electrical resistance of these two samples has estimated in a glass desiccator for several days.

The electrodes were two platinum-black plates 2×2 cm in size. They were fixed keeping them at a distance of 3 cm from each other in fish meat gruel. In this case, the specific electrical resistance was not estimated, but the apparent electrical resistance was estimated. The results are as shown in Table 35.

Table 35. Variation in the electrical resistance of fish meat gruel (Atka Mackerel meat) at certain intervals.

Processing \ Time (hrs)	0 hr.	15	21	63	87	111	135	159	183	231
(A) Antisepticized gruel by toluene	160Ω	160	155	185	180	170	170	175	170	170
(B) Non-antisepticized gruel	160	160	150	160	150	150	150	145	150	150
Remarks	pH {A. 6.3, B 6.6	6.3 6.6	— 6.4							pH {A. 6.4, B. 6.8

The electrical resistance of two samples (A) and (B) almost did not vary with the lapse of time after the handling. This result agrees with the results obtained by Tamura.

It was considered that the depression of the electrical resistance, that is to say, the increasing of electrical conductivity is not due to the increasing of the amount of the soluble matter by the autolysis of meat protein or the decomposition of meat protein by bacteria, but that it is due to the destruction of muscle tissue of the meat.

(C) The relation among the water-content in the putrefied fish meat, the electrical resistance and the distance of the electrodes.

From the previous two experiments, it was observed that the electrical resistance decreased with the destruction of the muscle tissue of fish meat.

Here, the present author has undertaken to study the relation among the water-content in the putrefied fish meat in the incipient drying, the electrical resistance and the distances of the electrodes.

The samples were fresh raw Atka Mackerel meat filet (11 × 1.5 × 1.0 cm) and the whole body of a species of Surf-smelt (*Hypomesus japonicus*), (10 gm in weight, 13 cm in length).

The distance between electrodes was 1.5 cm to 10 cm. The electrical resistances were observed for the samples two times in the incipient drying, and were observed thereafter for the putrefied samples which were laid at 30°C in the Petri dishes and began to have tainted smell. The putrefied fish meat was detected by Amano's $HgCl_2$[48] reaction. The electrical resistance of those samples was estimated at various water-content during the air drying. The estimation of the electrical resistance for the whole body of Surf-smelt was carried out as follows: two electrodes were thrust through into the center part of fish body between the surface of the body and back bone at the lateral line, and the electrical resistance was estimated at various distances of electrodes.

The experimental results are shown in Table 36 and 37. The average value of three samples is tabulated. The relation between the electrical resistance and the distance of electrodes is illustrated in Fig. 38, and the relation among

Table 36. Relation among the water contents in the putrefied Atka Mackerel meat, the electrical resistance (50 cycles) and the distance of electrodes.

Water Content (%) \ Distance of Electrodes (cm)	1.5cm	2.0	3.0	3.7	4.7	5.4	6.1	6.9	8.0	9.0	10.0	Remarks
75 %	KΩ 0.163	0.178	0.194	0.228	0.268	0.298	0.305	0.330	0.378	0.453	0.485	Drying
72.6	0.176	0.167	0.218	0.258	0.295	0.331	0.363	0.376	0.416	0.448	0.495	〃
70.0	0.208	0.238	0.256	0.296	0.325	0.371	0.402	0.427	0.498	0.546	0.605	〃
60.4	0.141	0.154	0.234	0.236	0.285	0.344	0.366	0.442	0.507	—	0.757	(Putrefied)
50.3	0.163	0.217	0.345	0.410	0.479	0.563	0.656	0.503	0.979	1.393	1.550	Drying

Table 37. Relation among the water contents in the putrefied meat of a species of Surf-smelt (Whole Body), the electrical resistance (50 cycles) and the distance of electrodes.

Water Content (%) \ Distance of Electrodes (cm)	1.5 cm	2.0	3.5	5.0	6.0	Remarks
75.4 %	0.390KΩ	0.380	0.535	0.663	0.813	Drying
72.5	0.390	0.415	0.550	0.738	0.825	〃
69.4	0.430	0.502	0.728	0.988	1.240	〃
64.7	0.366	0.393	0.638	0.913	1.192	(Putrefied)
55.7	0.421	0.457	0.866	1.373	2.085	Drying
40.3	0.640	0.817	1.618	5.325	30.533	〃
25.0	1.708	2.255	43.25	778	8,000 over	〃

Fig. 38. Relation among the electrical resistance (50 cycles), the distance of the electrodes and the total water content in fish meat in various conditions

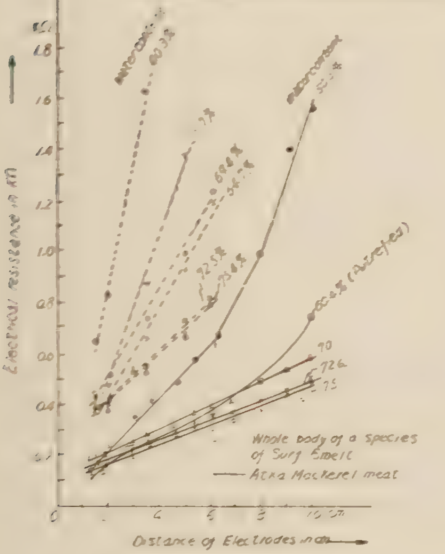
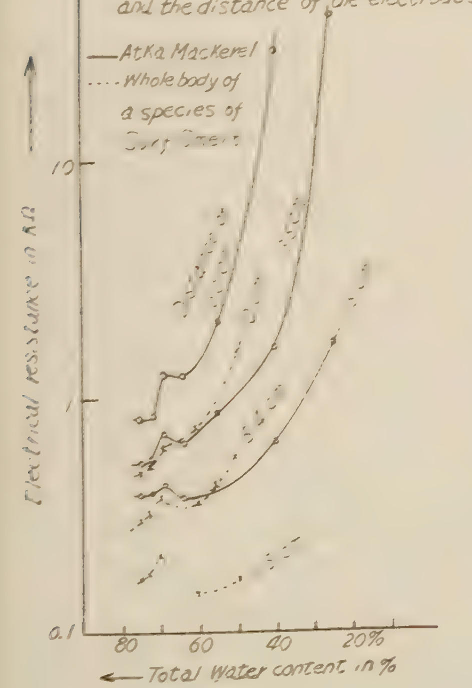


Fig. 39. Relation among the water contents in the putrefied fish meat, the electrical resistance and the distance of the electrodes.



the electrical resistance, the water-content and the distance of electrodes is illustrated in Fig. 39.

From Fig. 38, it was observed that the relation between the electrical resistance of Atka Mackerel meat and the distance of the electrodes was a linear function, and with the drying of meat the straight line slipped off upwards. But the electrical resistance of the completely putrefied Atka Mackerel meat (water-content 60 4%) depressed temporarily with the decreasing of water content and the linear function was not observed in the relation of the electrical resistance and the distance of the electrodes. This fact is perhaps due to the destruction of the muscle tissue of the fish meat. But the electrical resistance increased with the progressive drying of the putrefied fish meat. Then the straight linear showing of the relation between the electrical resistance of electrodes slipped off upwards. At excessive drying, the electrical resistance increased logarithmically as indicated in Fig. 39.

The straight line showing the relation between the electrical resistanc of Surf-smelt and distance of electrodes slipped off upwards at the upper part of the line with the drying. But the electrical resistance of the putrefied fish meat decreased temporarily with the decreasing of the water-content, then it increased logarithmically with the drying.

The electrical resistance of the drying fish meat without becoming putrefied could

be estimated. However, supposing from Figs. 38 and 39 showing the comparison of the curves of electrical resistance at the beginning of drying with after the putrefaction, the curve of the electrical resistance of the dried fish which was dried from fresh raw meat without putrefaction, perhaps slips off left from the curve of the electrical resistance of the putrefied meat. As stated in Experimet Ⅲ, 1[38a] of the previous paper, if the rapid ascending of the curve of the electrical resistance in the small water-content of the sample is due to the change of the amount of Bound Water in fish meat, the rapid ascending point of the curve of the electrical resistance of the putrefied fish meat may indicate lower water-content than in the fresh raw fish meat.

These facts are perhaps due to the decreasing of the amount of Bound Water or to the weakening of binding strength of Bound Water included in the same total amount of water in the sample, owing to the destruction of muscle tissue of fish meat. However, that the change of the electrical resistance varies with the change of pH value of the fish meat is also considered as one of the cause in this case. So the conclusion on the cause of these facts must be taken into further consideration.

(Ⅱ) Results of observation of the electrical resistance of 50 cycles in fresh meat, salted meat and putrefied meat of Atka Mackerel at various water-contents.

In this experiment, use was made of fresh raw Atka Mackerel meat (8×1.8×1.0 cm), putrefied Atka Mackerel which has a slight putrefied smell in incipient drying and in the same size, and brine-salted Atka Mackerel meat which has been immersed in saturated NaCl solution for 5 hours. The distance between the electrodes was 1.5cm. The observed results of the electrical resistance of 50 cycles at various water-contents are shown in Tables 38 and 39. The results on the amount of Bound Water for the same samples by the cobaltous chloride method are also shown in the same Tables. The results shown in Table 38 were the results in the case of drying at 19°C, and in Table 39 in that of drying at 20°∼30°C.

The temperature at which observations were made for all the samples was 17°C. Fig. 40 was derived by plotting the results in Tables 38 and 39.

From Fig. 40 it is observed that the electrical resistance of the raw fresh Atka Mackerel decreased with the incipient decreasing of the total amount of water during the drying of the fish meat at 19°C, and then the electrical resistance increased gradually at the neighbourhood of the water-cotent at the point B.P. which indicated the blue change point by the cobaltous chloride method (Oyagi's method), and the

Table 38. Relation between the electrical resistance (50 cycles) and the water contents in fresh, salted and putrefied Atka Mackerel meat. (Drying temp. 19°C)

Fresh Raw Meat		Salted Meat		Putrefied Meat		Putrefied Meat (Continued)	
Total Water Content (%)	Electrical Resistance (KΩ)	T. W. (%)	E. R. (KΩ)	T. W. (%)	E. R. (KΩ)	T. W. (%)	E. R. (KΩ)
79.6	0.45	70.2	—	79.1	0.455	15.1	50.0
70.3	0.41	64.2	0.035	74.0	0.340	14.5	135.0
48.4	0.45	55.2	0.045	68.6	0.450	14.0	160.0
38.2	0.65	52.0	0.049	60.9	0.400	12.9	279.0
24.5	5.50	45.6	0.060	49.6	0.420	12.4	300
20.2	60	40.0	0.110	37.4	0.500	10.2	7,000
14.8	1,000 over	31.0	0.260	29.4	1.23	—	—
—	—	21.2	65.0	17.0	3.23	—	—

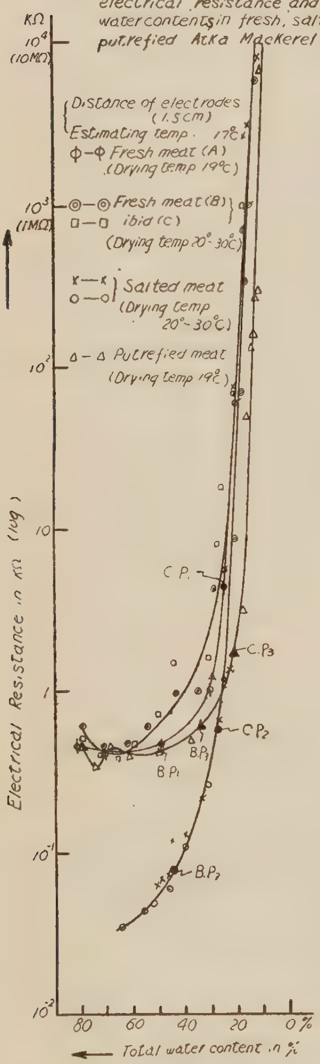
Total Water 79.6%	Total Water 70.2%	Total Water 79.1%
Free Water 60.0%	Free Water 46.3%	Free Water 68.6%
at B. P_1 { Bound Water 19.6%; g* 0.961	at B. P_2 { Bound Water 23.9%; (g)* 0.808	at B. P_3 { Bound Water 10.5%; (g)* (0.503)
at C. P_1 (g)* (0.372)	at C. P_2 (g)* (0.358)	at C. P_3 (g)* (0.280)
	Ash content 16.6%	
	NaCl 〃 15.7%	

* g = gm of Bound Water per gm of dried matter.

Table 39. Relation between the electrical resistance (50 cycles) and the total water contents in fresh and salted Atka Mackerel meat. (Drying temp. 20°~30°C)

Fresh Raw Meat (A)		Fresh Raw Meat (B)		Salted Meat	
Total Water (%)	Electrical Resistance (KΩ)	T. W. (%)	E. R. (KΩ)	T. W. (%)	E. R. (KΩ)
78.8	0.60	78.4	0.52	70.7	—
70.2	0.45	71.6	0.40	52.0	0.05
61.7	0.47	64.8	0.38	49.6	0.065
54.1	0.60	68.9	0.46	48.4	0.070
43.1	0.95	50.2	0.72	45.6	0.075
34.6	1.00	43.9	1.50	44.3	0.120
28.2	4.20	30.5	1.60	39.1	0.130
20.9	8.50	27.1	8.00	33.5	0.220
18.0	70.0	25.8	18.0	25.4	0.66
17.4	360	21.9	70	22.1	1.35
16.8	700	17.4	1,000	20.2	76
12.8	6,500	—	—	16.6	270
—	—	—	—	14.7	3,000
—	—	—	—	11.45	8,000

Fig. 40 Relation between the electrical resistance and the water contents in fresh, salted and putrefied Atka Mackerel meat.



resistance increased rapidly at the point of C. P. which indicates the constant-weight of the sample during the drying at 30°C. The curves showing the electrical resistance of two samples of the raw fresh Atka Mackerel are also almost the same curves during the drying at 20°~30°C.

However, the electrical resistance of the raw fresh meat dried at 20°~30°C was larger than that of the raw fresh meat dried at 19°C at the same water-content in 10~20% of the range of the water-content.

The higher the temperature is at the time of the observation, the smaller the electrical resistance is. The difference of the electrical resistance at the same water-content was considered to be due to the different drying temperatures, because the temperature at time of observation was the same after leaving the samples in the desiccator at 17°C for some time.

There is a factor, pH influencing the value of electrical resistance of the samples. The electrical resistance shows generally the maximum value at the iso-electric point of muscle protein. However, the value of pH of the fish meat is not considered to vary owing to the difference of the drying temperatures (the average difference of temperature is 5°C) which were employed in the experiment above described. The difference of the electrical resistance may better be considered to be due to the difference of the muscle tissue as affected by the drying temperatures. The muscle tissue of the fish meat dried at 19°C is rather homogeneous and closed by the gentle evaporation of water, but the muscle tissue of the fish meat dried at 20°~30°C has some gaps containing no water in the muscle tissue because of the more rapid evaporation. Therefore the electrical conductivity decreases and the electrical resistance increases.

The ascending of the curve of the electrical resistance of the sample dried at 20°~35°C below 20% of the water-content agrees with the sample dried at 19°C,

so there is rather little change of the amount of Bound Water in the two samples of fish meat dried at 19°C and at 20°～30°C.

In the putrefied meat, the property of the curve of the electrical resistance of the sample is the same as the curve in the case of raw fresh meat. The electrical resistance began to decrease at the water-cotent of the point of $B.P_3$ by the cobaltous chloride method, and increased rapidly at the point of $C.P_3$. However, the values of electrical resistance of the putrefied fish meat at various water-contents were lower than those of the raw fresh meat. Therefore, the curve of the putrefied fish meat slips wholly away from the curve of the raw fresh fish meat as expected from the preliminary experiment. Furthermore the amount of Bound Water of the putrefied fish meat at the points of $B.P_3$ and $C.P_3$ was less than that of the raw fresh fish meat at $B.P_1$ and $C.P_1$. This fact is perhaps due to the decreasing of Bound Water in the meat owing to the decomposition of the muscle tissue. However, the cause of this fact can not be concluded without clearing the relation between the change of the amount of Bound Water and the change of the value of pH with the putrefaction of fish meat.

In the salted fish meat, there is little difference in the electrical resistance of the samples dried at 19°C or at 20°～30°C. The salted fish meat contains an abundant amount of NaCl as the electrolyte in the fish meat (about 25% of the dried matter of the sample). Its electrical resistance is less than the raw fresh fish meat in the beginning of the estimation, but the electrical resistance increased rapidly with the lapse of the time of drying, and at last the ascending of the curve agreed almost with the curve of the raw fresh fish meat.

Suppoing that fish meat is a colloidal system consisting of water and protein, a part of the water in Bound Water which has weak strength to combine with protein hydrates with the elctrolyte, NaCl, by the addition of NaCl, and there perhaps remains only water which has strong ability to combine with protein. Therefore the electrical resistance was considered to increase rapidly by the remarked influence of combining strength of Bound Water with the decreasing of water in the course of the drying.

3. **Conclusion as to the results of estimations of the amount of Bound Water in the various states of meat of various kinds of fish by the cobaltous chloride method and by the measurement of the electrical resistance.**

The author has estimated the amount of Bound Water in the meat of various kinds of fish by the cobaltous chloride method (Oyagi's method) and by the measurement of the electrical resistance, and the following results and considerations were obtained.

(1) The amounts of Bound Water in the fresh raw meat of 12 kinds of fish were estimated; they differed with the kind of fish and individual bodies used, but it was recognized that the maximum amount of Bound Water is 55~82 gm, the minimum amount of Bound Water is 10~48 gm per 100 gm of the dried matter of the sample.

(2) From the estimated results of the amount of Bound Water, the absolute value of the amount of Bound Water decreased with the decreasing of the total amount of water during the drying of fish meat. The amount of Free Water in the total amount of water in the fish meat decreases from the beginning with the drying of the meat. But the amount of Bound Water increased relatively to the decreasing of the amount of Free Water at the incipient decreasing of the total amount of water in fish meat. The maximum value of the amount of Bound Water is observed as 40~50% of the total amount of water in fish meat, and then the amount of Bound Water decreased with the decreasing of the total amount of water in fish meat.

(3) The total amount of fish meat decreased by osmotic dehydration during and after salting. In this case, the percentage of the amount of Free Water decreased with decreasing of the percentage of the total amount of water and the percentage of the amount of Bound Water per gm of the dried matter with the decreasing of the weight of the dried matter of fish meat was not recognized during the salting. However, the amount of Bound Water is considered geneally to decrease.

(4) In this case of the decomposition of fish meat, e. g. in the putrefaction or in the fermentation of Squid meat (Soused Squid meat), it was observed that the percentage of the total amount of water increased gradually, the percentage of the amount of Free Water increased also, while the percentage of the amount of Bound Water decreased relatively. These results were observed to be different from the results influenced dehydration during the drying and salting. But in this case, the change of the absolute amount of Bound Water

was not clearly recognized by the cobaltous chloride method.

(5) During the autolysis or the putrefaction of fish meat, the electrical resistance decreased rapidly. This fact is considered to be due to the decomposition of the muscle tissue of the fish meat. And it was also observed that the larger the amount of Bound Water in fish meat was, the higher the electrical resistance was.

(6) Under this consideration, from the relation between the electrical resistance of fresh raw fish meat and putrefied fish meat and the amount of water in fish meat, the amount of Bound Water was considered to decrease with putrefaction.

(7) From the estimated results of the electrical resistance at various water-contents in the fresh raw fish and salted fish meat, it was supposed that when a large amount of NaCl penetrates into the fish meat, a part of the amount of Bound Water, except Bound Water possesing strong combining strength, hydrates with the added electrolytes (e. g. NaCl).

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(水產科學研所究業績　第 91 號)

STUDIES ON THE EXTRACTION OF FISH LIVER OIL.

I. EXAMINATION ON VITAMIN A CONTAINING FISH LIVERS AND ITS METHOD.

By

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With 3 tables

As the result of the simplification in the manner of determining vitamin A and D in liver oil it is possible to produce liver oil from other fishes as well as from cod which had been the only raw material for this purpose until rather recently. The writers attention was directed towards other fishes for liver oil production in which the extraction is easy bringing about remarkable progress in the liver oil industry.

Although there are many methods used in the manufacturing of liver oil, the one used here is the alkaline method the most commonly adopted in Japan. The authors proceeded to ascertain from which fish liver and by what method of extraction they could produce the highest vitamin content, maximum quality liver oil. This paper reports the results of several of these tests which are intended to make clear which fish contains higher or the highest unit vitamin A in its liver oil.

I. Relation between Changing pH with Oil Extraction and Vitamin A Unit.

METHOD:……Cut fish liver finely with a chopper. In the case of flounder *Reinhardtius matsuurae Jordan et Snyder*, all internal organs are used instead of liver only. Take a part of this finely minced material into a large container, after mixing thoroughly, and then 20 gr. of sample into a 100 c.c. Erlenmyer's flask. Add 20 c.c. of distilled water and mix well. By adding different quantities of 10% NaOH solution to the samples, different water solutions in value of pH are produced. Place the sample on a water bath, under constant shaking heat it to 50° C., which it to be maintained for one hour in the same condition, then raise the temperature to 85° C., and heat it at this temperature for another one hour.

The livers or organs are then completely dissolved. Take it off and cool it. Transfer the content into a separating funnel and refined peroxide-free ether. After thoroughly shaking, separate the upper and the lower layers from each other, the former into a Erlenmyer's flask. Repeat this operation several times and add all the upper layers together. The combined upper layers are then to be dehydrated with anhydrous Na_2SO_4. In separating, when the separation of ether layer from water layer is not clear, drop in a small quantity of ethyl alcohol. Shake a few minutes, set it aside, the layers will separate from each other completely. Next filler it into a weighed Erlenmyer's flask, evaporate the ether from the filtrate by warming it on a water bath at 30°–40°C., the residual Na_2SO_4 is washed with ether using $SbCl_3$, dissolve in $CHCl_3$ solution other indicator until the washing ether is colorless. The ether used for washing is added to the filtrate and the mixture is heated to drive away ether. Any ether and alcohol that may remain are freed from the filtrate by using vacuum pump.

RESULTS:……Table I shows the extraction of vitamin A from flounder. When pH value was between 11.3 to 13.0 there was no increasing of vitamin unit with increasing of pH value. On the contrary, oil extraction ratio gradully decreased.

Table 1

Tests No.	Liver quantity gr.	pH value	Oil quantity gr.	Ratio of oil extracted %	Vitamin A unit (U.S.P.U.)	Total vitamin A quantity in extracted oil (G.U.S.P.U.)	Total vitamin A quantity per gr. of internal organs (G.U.S.P.U.)
1	20.0	11.3	2.1	10.5	99100	208110	10405.5
2	20.0	12.0	1.9	9.5	99200	188480	9424.0
3	20.0	13.0	1.8	9.5	99400	178920	8946.0

II. On the Quantity of Liver Oil from Fish Livers and the Vitamin A Units in Those Liver Oils

METHOD:……(A) Adjust the pH of several different fish livers at values up to pH 11.4, under frequent shaking heat each of them at 50°C., for one hour and then one hour at 85°C. After complete dissolving, extract the oil with ether. The results are shown in Table II.

METHOD:……(B) Extraction of oil from livers directly without dissolving it with any alkali. Take 10 gm. of finely chopped fish livers into a mortar and add 50 gr. of anhydrous Na_2SO_4 to 5 times its weight. Mix well. Keep in a desiccator for a certain number of hours (about 2 to 3 hours) to dehydrate. Transfer into an Erlenmyer's flask, add ether, shake it, and set it aside. Filter the upper clear portion into a weighed flask. Repeat several times until the filtrate is

colorless when $SbCl_3$ dissolved in $CHCl_3$ solution is added. Put all portions of filtrate together and warm on a water bath at 30° to 40° C. to evaporate ether, then under vacuum pump drive away the last traces of any ether. The results are shown in Table III.

RESULTS:……Results obtained by the above methods are shown in the following tables. Table II shows the results of alkaline method when applied to small tuna, middle tuna *Thynnus thynnus Linne*, swordfish *Xiphias gladius Linne*, flounder and rockfish *Sebastolobus macrochir (Güntner)* together with equal quantities of flounder and rockfish. Table III shows the results from the direct ether extraction method. Raw materials used in this experiment are swordfish, middle tuna, mackerel *Scomber japonicus Houttuyn* and young tuna.

Table II

Species of fish	Liver quantity gr.	Water quantity cc.	5% NaOH cc.	NaOHgr. / liver %	pH value	Oil quantity gr.	Ratio of oil extracted %	Vitamin A unit (U.S.P.U.)	Total vitamin A quantity per gr. of livers (G.U.S.P.U.)
Small tuna	10.5	10.0	4.0	1.9	11.4	0.55	5.2	203000	10556.0
Middle tuna	10.0	10.0	4.0	2.0	11.4	0.50	5.0	860000	43000.0
Swordfish	10.0	10.0	4.5	2.2	11.4	1.00	10.0	245400	24540.0
Flounder	10.0	10.0	4.0	2.0	11.4	1.60	16.0	52200	8352.0
Rockfish	10.0	10.0	4.5	2.2	11.4	1.70	17.0	72700	12359.0
Flounder and Rockfish	10.0	10.0	4.2	2.1	11.4	1.70	17.0	67000	11390.0

Table III

Species of fish	Liver quantity gr.	Na_2SO_4 quantity gr.	Oil quantity gr.	Ratio of oil extracted %	Vitamin A unit (U.S.P.U.)	Total vitamin A quantity per gr. of livers (G.U.S.P.U.)	Extinction ratio E 300/328
Swordfish	10.0	50.0	1.50	15.0	33500	5025.0	173.6
Middle tuna	20.0	100.0	1.10	5.5	142200	7821.0	108.8
Mackerel	20.0	100.0	1.05	5.3	111100	5888.3	——
Young tuna	10.0	50.0	0.60	6.0	46800	2808.0	——

As clear from the above tables tuna are classified as large tuna, middle tuna and small tuna, the vitamin A unit of the former is much higher than that of the latter. The vitamin A unit of flounder is relatively low, yet its oil extracting ratio is much great. The vitamin A units of mixture of equal quantities of flounder and rockfish indicate that its vitamin A unit seems to be more abundant in comparison with the results of extracting them separately.

From Table III, the oil extraction ratio of swordfish is seen to be high while the others show no difference. Materials used in Table II and that used in Table III are not the same which makes the comparison of data in these two tables impossible. The different conditions of livers, for instance their freshness and the

method of treatment used, will influence the results greatly even though the livers are of the same kind of fish.

III. Conclusion

(1) When the extraction is applied to livers dissolved with alkalis, i. e., when the solution is adjusted at pH 11.3 to 13.4, the vitamin A unit of the liver oil will increase with the increasing pH value, while contrariwise the oil extracting ratio decreases at the same time.

(2) Livers of tuna, rockfish and swordfish and internal organs of flounder contain high vitamin A unit.

（水產科學研究所業績　第 92 號）

STUDIES ON THE EXTRACTION OF FISH LIVER OIL.

II. THE EXTRACTION OF OIL FROM FISH LIVERS CONTAINING HIGH VITAMIN A UNIT.

By

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With 5 tables

Introduction

Examining how to operate in order to produce an oil of high unit value and a high yield, the authors find that by using the generally adopted alkaline method and by stressing pH 11, the best result is obtained.[1]

The following is a report of the results of an industrial test with this method which it is hoped may be of some reference value.

I. Internal Organs of Flounder.

METHODS OF EXTRACTION OF OIL:-

A. Method of separating the upper layer......Weigh out flounder internal organs that were cleared as completely as possible of meat, bones, skins and other. Chop it finely and place it in a tank. After the stirrer is started, add water. The amount of water is determined by the hardness of the material (that is its frozen condition) when it is chopped and just placed into the tank as well as the content of the water used is generally 2 times the volume of the materials used. If it is to be transferred by gear pump into a tank at a higher position, the chopped material is first placed in a small tank with sufficient water to dilute it so that it can be pumped up. When it is too hard, water may be used. Then it can de handled in the same way. During or after chopping, add approximately 2% its weight solid caustic soda in Bé 15° to 25° solution directly to the tank or the small tank while stirring swiftly. This so adjusted that after it is completely transferred into the tank the resulting pH must be 11 to 12. Blow in steam and raise its temperature (preferable to use a double bottom pan) to dissolve it. While the temperature is increasing the material is also being dissolved with a result that its pH value will be lowered. This is to be adjusted by adding frequently a

small quantity of NaOH solution to maintain its pH at 11. At 50°C. take a portion of the solution in a beaker, set it a few minutes and see whether the dissolution is good or not. When it is good, raise its temperature above 50°C. and examine in the same way frequently. If this is not the case, maintain its temperature at 50°C. to 60°C. and stir all the while for half to one hour and then examine it. If the dissolution is still not good, add sufficient quantity of NaOH solution. Temperature is to be raised only after solid matter has been dissolved.

At 80° to 85°C. stir the mixture for about one hour until it is completely dissolved. Add water to lower its temperature to 50° to 60°C., then stop stirring and cover. Take out the emulsion including oil layer. Add 3 times its weight of hot water, separate by Sharpless' centrifugal machine, so crude oil is obtained.

B. Method of separating whole liquor......When the whole solution is to be centrifugated by a Sharpless' centrifuge, its dissolution is carried in the following manner: a certain amount of raw material is first chopped and placed in a small tank to which water is added at a ratio of 1:1 or less. This is then heated with alkali. The quantity of NaOH is a little larger than in the former case. Several minutes or more after its complete dissolution the whole material is transferred into a large tank from which the crude oil is obtained by using a Sharpless' centrifugal machine. This operation is repeated again and again.

RESULTS:-

In Table I, A shows the results in each month while B shows that on each day. Both tests were carried out in 1950. In Feb., March, April, July and August there was scarcely any flounder to be used for making liver oil, therfore, these columns are blanks. The amount of NaOH that would adjust the pH value at 11 to 12 was nearly 2.5% for each sample. Temperature of dissolution was 85°C. The necessary quantity of NaOH for complete dissolution seems to be dependent somewhat upon the freshness, quantity of water used, and other factors.

Though thermometric experiment was not carried out, it is clear from industrial test in factories that at a high temperature of about 100°C. vitamin A unit will be decreased by about 7%. Dissolution of raw materials will be better when its temperature is high, however 85°C. is the optimum in the authors' opinion. All experiments were therfore carried out at this temperature.

In December both vitamin A unit and oil quantity were high, yet this differed remarkably in accordance with the origin and the factory where the fish were treated. This increase both in units and in quantity in December may be accounted for from the fact that impurities in the organs are very low, the

weights of liver and pylorus are higher and the water content of organs is less than those of fish taken in other months.

The results obtained from the above two methods show no difference from one another. In other points except numerical relations, there may be some difference. For some reasons the total vitamin A quantity per gr. of internal organs show no remarkable change during seasonal changes. However, generally, it seems that the maximun quantity is obtained in December and in January. In the same period oil quantity will be less when higher quantity of NaOH is used, while vitamin A unit becomes high instead; when amount of NaOH used is lower, the contrary is true. The total vitamin A quantity per gr. of internal organs is the same influenced by the quantity of NaOH used. Raw materials in the same period will require different quantities of NaOH for their complete dissolution. This is owing to the difference in stocking usually at 85°C., for during that time these materials will undergo an autolysis. This autolysis, when occurring to a certain degree will lead to a better dissolution of the material and the total vitamin A quantity per gr. of internal organs will be slightly higher. However, fresh material will show good results in regard to odor, color, deterioration and

Table I A

Date	Internal organs quantity kg.	NaOH quantity of addition kg.	NaOH/Internal organs %	Oil quantity kg.	Ratio of oil extracted %	Vitamin A unit U.S.P.U.	Total Vitamin A quantity per gr. of internal organs G.U.S.P.U.	Method of extraction of oil	Fish market
Jan., 1950	5976.0	135.7	2.27	371.0	6.20	147000	9114.0	By method A	Siogama
Feb., 〃	——	——	——	——	——	——	——	——	——
Mar., 〃	——	——	——	——	——	——	——	——	——
Apr., 〃	——	——	——	——	——	——	——	——	——
May, 〃	7727.0	128.3	1.66	465.0	6.01	124000	7452.4	By method A	Siogama
〃 〃	8431.0	197.4	2.34	524.7	6.22	132000	8210.4	〃	〃
June, 〃	8222.0	288.0	3.50	452.0	5.49	103000	5654.7	〃	〃
July, 〃	——	——	——	——	——	——	——	——	——
Aug., 〃	——	——	——	——	——	——	——	——	——
Sept., 〃	5912.0	178.4	3.01	393.0	6.64	124000	8233.6	By method A	Siogama
Oct., 〃	5925.0	152.2	2.56	390.0	6.58	103000	6777.3	〃	〃
〃 〃	3309.0	89.0	2.68	224.0	6.77	98000	6634.6	〃	〃
〃 〃	2140.0	61.6	2.87	159.0	7.43	99300	7377.9	〃	〃
Nov., 〃	4272.0	159.3	3.72	276.0	6.46	105000	6783.0	〃	〃
Dec., 〃	7518.0	211.0	2.80	549.0	7.30	123000	8979.0	By method B but a part is by method A	Hatinohe
〃 〃	5040.0	125.6	2.49	372.5	7.39	139100	10279.0	〃	〃
〃 〃	10920.0	272.3	2.49	716.0	6.55	150000	9825.0	〃	〃
Total or average value	75392.0	1998.8	2.65	4892.2	6.48	124700	8080.5		

Table I B

Date	Internal organs quantity kg.	NaOH quantity of addition kg.	NaOH/ Internal organs %	pH value	Heating temperature °C	Oil quantity kg.	Ratio of oil extracted %	Acid value	Vitamin A unit U.S.P.U.	Total vitamin A quantity per gr. of internal organs G.U.S.P.U.
Feb. 27, 1950	1411.0	39.80	2.82	11	85	67.7	4.79	0.24	150000	7185.0
Feb. 28, ″	1577.0	34.62	2.19	11	85	95.6	6.06	0.55	147000	8908.2
Feb. 29, ″	1494.0	30.72	2.05	11	85	95.0	6.35	0.80	—	—
Feb. 30, ″	1494.0	30.61	2.04	11	85	113.0	7.56	1.10	—	—
May 2, ″	1859.0	22.77	1.22	11	85	125.6	6.75	0.52	109500	7391.2
May 4, ″	1843.0	24.94	1.35	11	85	117.0	6.35	0.30	—	—
May 5, ″	1857.0	24.12	1.29	11	85	92.4	4.97	1.80	—	—
May 6, ″	2168.0	56.55	2.60	11	85	130.0	5.99	0.40	130000	7787.0
May 9, ″	1762.0	38.62	2.19	11	85	107.0	6.07	—	122000	7405.0
May 10, ″	1724.0	40.88	2.37	11	85	114.0	6.61	—	—	—
May 11, ″	1907.0	45.00	2.35	11	85	122.0	6.39	—	—	—
May 12, ″	1480.0	35.84	2.42	11	85	94.0	6.35	—	—	—
May 13, ″	1459.0	34.34	2.35	11	85	80.7	5.53	—	—	—
May 15, ″	99.0	2.75	2.77	11	85	7.0	7.07	—	—	—
June 23, ″	1936.0	51.88	2.67	11	85	107.2	5.53	—	108700	6011.1
June 24, ″	1807.0	61.11	3.38	11	85	109.6	6.06	—	97000	5878.2
June 25, ″	1770.0	68.80	3.88	11	85	99.6	5.62	—	108000	6369.6
Sept. 20, ″	1679.0	50.40	3.00	11	85	112.0	6.67	0.30	119500	7960.6
Sept. 21, ″	3307.5	99.20	2.99	11 11	85 100	110.0 106.0	6.53	— —	130100 120900	8201.6
Oct. 13, ″	3121.0	79.80	2.55	11	85	196.0	6.28	0.46	109000	6845.2
Oct. 14, ″	1630.0	45.90	2.81	11	85	91.0	5.58	0.66	125000	6975.0
Oct. 19, ″	3309.0	89.00	2.65	11	85	224.0	6.76	0.40	98000	6624.8
Oct. 31, ″	2140.0	61.60	2.87	11	85	159.0	7.42	0.32	99300	7368.0

Table II A

Date	Species of fish	Liver quantity kg.	NaOH quantity of addition kg.	NaOH/ Liver %	pH value	Heating temperature °C	Oil quantity kg.	Ratio of oil extracted %	Acid value	Vitamin A unit U.S.P.U.	Total vittamin A quantity per gr. of liver G.U.S.P.U.
Oct. 1, 1949	Swordfish	145.7	2.91	2.00	11	85	11.6	7.96	—	119400	9432.6
〃 〃	Spearfish	29.0	0.75	2.50	11	85	0.6	2.06	—	171100	3422.0
Oct. 13, 1949	〃	164.0	7.00	4.26	11	85	4.3 (0.9)	2.62 (0.54)	—	125000	3375.0 (2781.3)
(Pick up oil of addition. Codfish liver oil Vitamin A unit 23930 U.S.P.U., 3.4 kg.)											
June 24, 1949	Rockfish	992.0	20.83	2.10	11	85	136.0	13.70	—	100000	13700.0
June 4, 1950	〃	533.0	15.51	2.90	11	85	44.0	9.25	1.30	120600	9949.5

Table II B

Date	Species of fish and liver quantity kg.	Total liver quantity kg.	NaOH quantity of addition kg.	NaOH/ Liver %	pH value	Heating temperature °C	Oil quantity kg.	Ratio of oil extracted %	Acid value	Vitamin A unit U.S.P.U.	Total vitamin A quantity per gr. of liver G.U.S.P.U.
June 24, 1949	Rockfish 151, Tuna 249, Swordfish 40,	535.0	11.23	2.09	11	85	45.0	8.41	—	130000	10933.0
Oct. 1, 1949	Middle tuna 67.1, Small tuna 274,	341.1	6.70	1.96	11	85	2.6	0.76	—	186500	1417.4
Oct. 5, 1949	Flounder 95, Swordfish 19,	114.0	5.00	4.38	11	85	10.0	8.77	1.68	117900	10257.3
Oct. 18, 1949	Rockfish 15.3, Middle tuna 50.8, Flounder 22.5, Big-eyedtuna 78.1, Spearfish 1323.1,	1489.8	50.00	3.35	11	85	96.9 (43.7)	6.50 (2.93)	—	120200	7813.0 (6723.5)
(Pick up oil of addition. Codfish liver oil vitamin A unit 23930 U.S.P.U., 44.7kg. and Spearfish liver No.2 oil vitamin A unit 66000 U.S.P.U., 8.5kg.)											
July 10, 1950	Flounder 96, Tuna 27,	123.0	4.80	3.90	11	85	8.0	6.42	—	107000	6869.4
Sept. 22, 1950	Flounder 782, Rockfish 112, Middle tuna 32,	926.0	49.00	5.29	11	85	69.0	7.45	—	127600	9506.2
Oct. 12, 1950	Flounder 738, Swordfish 128, Rockfish 198, Tuna 215,	1174.0	26.50	2.25	11	85	103.0	8.77	0.28	107500	9427.7
Oct. 20, 1950	Flounder 540, Rockfish 111,	651.0	17.60	2.70	11	85	53.0	8.14	0.30	96600	7863.2

Table II C

Date	Species of fish	Acid value	Vitamin A unit U.S.P.U.	Extinction ratio E 300/328
July 2, 1950	Rockfish, Swordfish, Middle tuna, Small tuna,	0.36	202000	——
July 3, 〃	Flounder, Rockfish,	0.44	100000	——
〃 〃	Flounder, tuna,	0.52	107000	——
July 4, 〃	Young tuna	0.41	70300	——
Sept. 10, 〃	Tuna	0.33	221000	65.7
〃 〃	Swordfish	0.40	423600	63.6
〃 〃	Flounder	0.30	132700	62.6
〃 〃	Flounder, Swordfish,	0.32	228000	63.6
〃 〃	Tuna, Swordfish,	0.36	220100	63.6

acid value.

II. Livers of Different Kinds of Fish.

METHOD OF EXTRACTION OF OIL:-

The same as described in I. Since high vitamin A content livers of fish other than flounder are generally hard in quality, they are again finely divided with a micronizer after having been finely chopped. Livers that are likely to have a lesser quantity of liver oil are treted with pick-up oil; the quantity of it has to be used in accordance with the amount of the original raw material to avoid lowering the quantity of vitamin A unit the resultant oil. For cod liver oil and No. 2 oil having a vitamin A units of 20,000 to 30,000 U.S.P.U. it is good to use about 3% of this transfer oil. It is added during stirring after complete dissolution of solid matters. Of course the stirring time must be somewhat prolonged in this case. When the extraction is performed with mixture of livers of different kinds of fish, each kind of liver is chopped in separate tanks and then mixed. Method of dissolution of the mixture is the same as described above.

RESULTS:-

In Table II A shows the oil extraction results with fish livers of different high vitamin A content fish except flounder and B that of mixture of livers of different kinds of fishes. While C shows only their acid values, vitamin A unit and extinction ratio for lacking sufficient livers for weighing purposes.

III. Summary

(1) At pH 11 to 12, though the amount of NaOH used for dissolution is somewhat dependent upon the freshness of raw materials used and the amount of water used in dissolution, it is generally about 2.5% of the weight of the law materials.

(2) In industrial practice in factories, vitamin A unit will be higher while the oil quantity is less when NaOH used is more than that used generally; the contrary is true when less NaOH is used.

(3) In case of flounder, the total vitamin A quantity per gr. of internal organs is highest in December and January. Within the same period, its value is nearly the same without regard to the amount of NaOH used in dissolution of the material.

(4) In the extraction of oil from mixed raw materials, rather a good results were obtained.

IV. Literature

1) K. Murata and M. Suzuki (1951): Bull. Faculty of Fisheries, Hokkaido University, 2, 4, pp. 262-265

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STUDIES ON THE EXTRACTION OF FISH LIVER OIL.

III. THE EXTRACTION OF OIL FROM FISH LIVERS CONTAINING LOW VITAMIN A UNIT.

By

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With 5 tables

Introduction

The following report is an account of the authors efforts to find by what method or treatment is it possible to extract from low-vitamin-A-unit-content fish livers, such as those of codfish, shark, and bonito, a possibly higher vitamin-A-unit liver oil and in larger quantity. The authors used the alkaline method on an industrial scale with the above mentioned fish livers. They hope their report may be of some reference value at least.

I. Cod Liver and Its Internal Organs.

METHODS OF EXTRACTION OF OIL:—

Liver oils extracted from codfish livers and that from codfish liver together with the other internal organs, the so-called "whole internal organs", are quite different in their vitamin A unit, their odor, and their color. Generally, these raw materials were bought separately and used separately according to the purpose of their uses. The oil extraction operation was the same as the one described for extracting oil from high-vitamin-A-unit-content fishes in the authors' former report, namely, raw materials freed from impurities after weighing were chopped finely and placed in a tank for extraction.

Methods of extraction used were (A) Method of separating the upper layer, and (B) Method of separating the whole liquor.

(A) Method...... Quantity of water used was approximately 1 to 2 times the raw material used. When oil content is large, after emulsification, the milky white liquor will be quite abundant and will make the decantation difficult, the container inconvenient for use, and, moreover, its centrifugal separation will require much more time. However, codfish liver is soft in character and easy to

be dissolved. Add NaOH of 20° to 30° Bé to adjust pH of the material about 8.0 and heat it. When at 50°C., the raw material starts to decompose, if the operation is in a fair condition its temperature may be raised directly to 85°C., at which temperature water is added to lower the temperature to 50°–60°C. while the stirring also is stopped. Cover it and decant the upper oil layer the next morning. By centrifugal separation crude oil is obtained.

(**B**) **Method**......Use as small a quantity of water as possible and use some more NaOH than that used in Method A to adjust pH of material to 9 approximately. Then heat it. At 85°C., stop the stirring, transfer to a tank and separate either immediately or after being let stand quietly for several hours, to obtain crude oil centrifugally.

RESULTS:–

In Table I A, data cover a period from February 1948 to October 1950 during which period livers of pollack and that of codfish caught in all months excepting January and April were used for monthly tests. In February, September, October and November, 1950 fish were taken every day during a certain period. The results of daily tests with daily caught fish as samples are presented in Table I B.

From those results it is clear that when a great quantity of raw material is used and extracted with industrial equipment, the operation is convenient when

Table I A

Date	Species of fish	Liver quantity kg.	NaOH quantity of addition kg.	NaOH/Liver %	Oil quantity kg.	Ratio of oil extracted %	Vitamin A unit U.S.P.U.	Total vitamin A quantity per gr. of liver G.U.S.P.U.	Remarks
Feb., 1948	Pollack	343.0	5.0	1.4	103.0	30.0	3750	1125.0	
〃, 1949	〃	2078.0	45.0	2.1	670.0	32.2	——	——	
〃, 1950	Codfish	3578.0	45.2	1.2	1125.0	31.4	11480	3604.7	
Mar., 1949	〃	2894.0	55.2	1.9	716.0	24.7	——	——	
May, 1949	〃	509.0	11.5	2.2	113.0	22.2	16780	3725.1	
June, 1949	〃	4143.0	64.5	1.5	1161.0	28.0	17950	5026.0	
〃, 〃	〃	1784.0	22.5	1.2	441.0	24.7	11000	2717.0	
〃, 1950	Pollack	2119.0	48.7	2.2	781.0	36.8	1100	404.8	
July, 1949	〃	2859.0	60.0	2.0	680.0	23.7	9535	2259.7	
Aug., 1949	Codfish	1557.0	62.0	3.9	436.0	28.0	——	——	
Sept., 1949	〃	1515.0	62.0	4.0	437.0	28.8	——	——	
〃, 1950	Pollack	1257.0	29.0	2.3	332.0	26.4	7480	1975.4	Whole internal organs
Oct., 1950	〃	4074.0	114.0	2.7	741.0	18.1	8080	1462.4	
〃, 〃	〃	5761.0	176.4	3.0	922.0	16.0	7140	1142.4	
Nov., 1950	〃	8045.0	150.4	1.8	1528.5	18.9	6000	1134.0	
Dec., 1948	〃	828.5	15.5	1.8	270.0	32.5	——	——	

Table I B

Date	Species of fish	Liver quantity kg.	NaOH quantity of addition kg.	NaOH Liver %	pH value	Heating temperature °C	Oil quantity kg.	Ratio of oil extracted %	Vitamin A unit U.S.P.U.	Total vitamin A quantity per gr. of liver G.U.S.P.U.	Acid value	Remarks
Feb. 19, 1950	Codfish	789.0	9.7	1.22	8	80	230.0	29.15	11800	3439.7	2.5	By method A
Feb. 20, 1950	〃	986.0	12.0	1.21	8	80	307.6	31.19	11500	3586.8	3.2	〃
Feb. 21, 1950	〃	945.0	11.7	1.23	8	80	284.4	30.09	11500	3460.3	4.6	〃
Feb. 22, 1950	〃	858.0	11.8	1.37	9	80	303.0	35.31	11200	3954.7	2.9	〃
Sept. 22, 1950	Pollack "Whole internal organs"	1257.0	29.0	2.30	9	80	332.0	26.41	7480	1975.4	0.67	〃
Oct. 16, 1950	〃	2054.0	56.6	2.75	9	80	359.0	17.47	8160	1425.5	0.52	〃
Oct. 17, 1950	〃	2020.0	57.4	2.84	9	80	382.0	18.91	8000	1512.8	0.60	〃
Oct. 21, 1950	〃	1514.0	47.4	3.13	—	80	274.0	18.09	7480	1353.1	0.65	〃
Oct. 22, 1950	〃	4247.0	129.0	3.03	—	80	648.0	15.25	7000	1067.5	0.77	〃
Nov. 9, 1950	〃	862.0	24.6	2.85	9	85	151.0	17.51	4900	857.9	0.35	By method B
Nov. 10, 1950	〃	1140.0	20.1	1.76	9	85	237.8	20.85	5900	1230.1	0.30	〃
Nov. 11, 1950	〃	1515.0	27.7	1.82	9	85	304.2	20.07	8000	1605.6	0.25	〃
Nov. 13, 1950	〃	1623.0	28.7	1.76	9	85	266.4	16.41	6000	1312.8	0.31	〃
Nov. 14, 1950	〃	745.0	12.6	1.69	9	85	141.2	18.95	8000	1516.0	0.35	〃
Nov. 17, 1950	〃	900.0	16.3	1.81	9	85	182.6	20.28	7700	1561.5	0.27	〃
Nov. 18, 1950	〃	1260.0	20.4	1.61	9	85	245.3	19.46	7900	1537.3	0.40	〃

(A) Method is used. As to the adjustment of pH, it seems that the result is somewhat better when material is adjusted to pH 9.0 rather than 8.0 and then heated, though from the view point of centrifugal separation the latter pH value is preferable. For samples of the same period, when the pH values were adjusted to 8.0–9.0, the quantity of NaOH used was almost the same in each case, i.e., about 2%. Liver oil from pollack or from codfish is light yellow in color, of relatively less odor, and a good oil extracting ratio; its vitamin A unit is also 10,000 U.S.P.U. Liver oil from the whole internal organs has a light red color, of an unpleasant odor, and a rate of oil extraction inferior to that of the former case. Its vitamin A unit is less than 10,000 U.S.P.U. Raw materials obtained in the same period seen to have an equal total vitamin A quantity per gr. of liver regardless of which extraction method is used.

II. Shark Livers.

Liver oils of great blue shark and salmon shark have generally a vitamin A unit of 3,000 U.S.P.U.; they contain

carbohydrates and waxes for which reason their melting points are high and their degrees of transparency at lower temperatures are not good. They are difficult to be refined and, therefore, are unsuitable as a source of vitamin A oil. Hence, stress is placed technically on a high quantity of oil extracted and a simpler operation rather than on its vitamin A unit. However, in the liver oil of codfish, though its vitamin A unit differs according to the color of the liver, its vitamin A concentration is usually 20,000 to 40,000 U.S.P.U. In this case, care must be taken, as in the case with high-vitamin-A-unit fishes, to extract the oil by heating in order to obtain a higher vitamin-A-unit product in larger quantity.

METHOD OF EXTRACTION OF OIL:–

Free impurities from the raw material; after weighing, chop finely with a chopper and transfer it into a tank. Extraction of oil is then performed by either method (A), separating of the upper layer or by (B), separating of the whole liquor.

RESULTS:–

Table II A presents the monthly test results from fish taken in each month during a period from February 1947 to September 1950; B reports on a period from June to December 1949. Data indicated as "shark" only, are results obtained from a mixture of both great blue shark and salmon shark. Amount of solid NaOH used with these two kinds of shark livers was generally about 1%; the same percentage of NaOH was also used with dogfish. Quantities extracted were about 40% for the former two kinds and about 50% for dogfish. Vitamin-A-units were 3,000–6,000 U.S.P.U. and 8,000–15,000 U.S.P.U. respectively.

Some of the dogfish livers were black and some were white in color. They were sampled separately and their vitamin A units determined separately. It is clear that the black had much more vitamin A than the white livers, being about 40,000 U.S.P.U., twice that of the latter.

During the operation, care must be taken to note that, during transportation in summer from the seashore where fish were taken to the oil extraction plant, the oil would separate out of itself. This would be more evident when it was kept in the factory and the longer the period of keeping the more oil would be separated out which would then float on the surface of the container. This self-separated oil had to be transfered separately to another container before livers were chopped. This oil might be kept separately after weighing or added to the

Table Ⅱ A

Date	Species of fish	Liver quantity kg.	NaOH quantity of addition kg.	NaOH/Liver %	Oil quantity kg.	Ratio of oil extracted %	Vitamin A unit U.S.P.U.	Total Vitamin A quantity per gr. of liver G.U.S.P.U.
Jan., 1949	Shark	1996.0	50.5	2.5	825.0	41.3	——	——
Feb., 1947	〃	929.0	12.6	1.3	320.0	34.4	——	——
〃 , 1948	Great blue shark Mackerel shark	456.0	7.0	1.5	182.0	39.9	——	——
〃 , 1949	Shark	3577.0	73.0	2.0	1389.0	38.8	4300	1668.4
Apr., 1947	〃	243.0	0.8	0.3	75.0	30.8	——	——
May, 1948	〃	172.0	1.7	0.9	45.0	26.1	——	——
〃 , 1949	〃	460.0	2.5	0.5	205.0	44.5	6290	2799.5
〃 , 1950	Dogfish shark	65.0	1.0	1.5	45.0	69.2	8700	6020.4
June, 1949	〃	6004.0	56.0	0.9	3509.0	58.4	5000	2920.0
〃 , 〃	Shark	4521.0	68.7	1.5	1620.0	35.8	——	——
〃 , 1950	〃	22.0	0.5	2.2	6.0	27.2	——	——
July, 1947	〃	234.0	2.1	0.8	80.0	34.1	26400	9002.4
〃 , 1949	〃	5402.0	79.5	1.4	1984.0	36.7	——	——
〃 , 1950	Degfish shark	722.0	36.0	4.9	387.0	53.6	2250	1206.0
Aug., 1947	Shark	5103.0	16.5	0.3	1224.0	23.9	3300	788.7
〃 , 1948	Salmon shark	2229.0	50.7	2.2	631.0	28.3	——	——
〃 , 1949	Dogfish shark	753.0	13.0	1.7	300.0	39.8	——	——
〃 , 〃	Shark	17740.0	245.5	1.3	6776.7	38.2	——	——
Sept., 1947	〃	1200.0	7.1	0.5	530.0	44.1	6900	3042.9
〃 , 1948	Great blue shark	814.0	13.2	1.6	237.0	29.1	——	——
〃 , 1949	Dogfish shark	1424.0	12.3	0.8	739.0	51.8	——	——
〃 , 〃	Shark	5118.0	47.5	0.9	2047.2	40.0	——	——
〃 , 1950	〃	148.0	2.0	1.3	60.0	40.5	——	——
Oct., 1947	〃	613.0	4.9	0.7	261.0	42.5	——	——
〃 , 1949	〃	11304.0	108.1	0.9	5016.0	44.3	——	——
Nov., 1947	〃	979.0	10.0	1.0	386.0	39.4	3600	1418.4
〃 , 1948	Etmopterus shark	2710.0	11.5	0.4	1980.0	73.0	——	——
〃 , 〃	Shark	4828.0	76.2	1.5	1540.0	31.8	——	——
〃 , 〃	Hammer head shark	234.0	2.5	1.0	90.0	38.4	60000	23040.0
〃 , 1949	Dogfish shark	6583.0	81.4	1.2	3725.0	56.5	22000	12430.0
〃 , 〃	Shark	14066.0	158.7	1.1	7055.0	50.1	——	——
Dec., 1947	Dogfish shark	184.0	1.7	0.9	92.0	50.0	14400	7200.0
〃 , 1948	〃	483.0	8.8	1.8	212.0	43.8	1200	525.6
〃 , 1949	〃	2368.0	28.0	1.1	1170.0	49.4	——	——

Table Ⅱ B

Date	Species of fish	Liver quantity kg.	NaOH quantity of addition kg.	NaOH/Liver %	pH value	Heating temperature ℃	Oil quantity kg.	Ratio of oil extracted %	Vitamin A unit U.S.P U.	Total vitamin A quantity per gr. of liver G.U.S.P.U.	Acid value	Fish market
June 28, 1949	Shark	1330.0	18.8	1.41	8.6	80	498.0	37.44	—	—	—	Siogama
〃 29, 〃	〃	1530.0	25.0	1.63	9.2	80	582.0	38.04	—	—		〃
July 20, 〃	〃	1513.0	25.0	1.65	9.4	80	570.0	37.67	—	—	—	〃
〃 21, 〃	〃	1648.0	27.5	1.66	9.4	80	680.0	41.26	—	—	—	〃
Aug. 16, 〃	〃	2145.0	20.6	0.96	9.0	80	700.0	32.63	—	—		〃
〃 17, 〃	〃	2145.0	15.0	0.69	8.6	80	692 0	32.26	—	—	—	〃
〃 18, 〃	〃	2150.0	26.5	1.23	9.6	80	1075.0	50.00	—	—	—	〃
Sept. 22, 〃	〃	1379.0	10.9	0.79		80	514.0	37.27	—	—	-	Nemuro
〃 23, 〃	〃	1556.0	11.5	0.73	—	80	684.0	43.65	—	—	—	〃
〃 24, 〃	Dogfish shark	1424·0	12.3	0.86	—	80	739.0	51.89	—	—	—	〃
Oct. 25, 〃	Shark	1244.0	11.4	0.91	9.6	80	528.0	42.42	—	—	—	Hatinohe
〃 26, 〃	〃	1588.0	14.3	0.90	9.2	80	732.0	46.09	—	—	—	〃
〃 27, 〃	〃	1575.0	12.6	0.80	—	80	771.0	48.95	—	—	—	〃
〃 28, 〃	〃	1568.0	17.7	1.12	—	80	797.0	50.82	—	—	—	〃
〃 29, 〃	〃	857.0	10.6	1.23	—	80	436.0	50.87	—	—	—	〃
Nov. 1, 〃	〃	1595.0	17.9	1.12	—	80	697.0	43.69	—	—	—	〃
〃 2, 〃	〃	1947.0	19.2	0.98	—	80	957.0	49.15	—	—	-	〃
〃 3, 〃	〃	2010.0	18.6	0.92	—	80	1074.0	53.43	—	—	—	〃
〃 17, 〃	Dogfish shark "white liver"	1175.0	8.0	0.68	-	80	685.0	58.29	17700	10317.3	0.9	Nemuro
〃 18, 〃	〃	1853.0	10.6	0.57	—	80	1015.0	54.77	—	—	1.8	〃
〃 19, 〃	〃	1832.0	30.4	1.65	—	80	849.0	46.34	—	—	0.7	〃
〃 20, 〃	〃	1143.0	22.3	1.95	—	80	583.0	51.00	22690	11571.9	0.4	〃
〃 〃 〃	Dogfish shark "black liver"	575.0	9.1	1.58	—	80	243.0	42.26	44060	18619.7	-	〃
Dec. 23, 〃	Shark	1480.0	20.0	1.35	—	80	667.0	45.06	—	—	—	Hatinohe
〃 24, 〃	〃	888.0	8.4	0.94	—	80	418.4	47.11	—	—	—	〃

Table III

Date	Liver quantity kg.	NaOH quantity of addition kg.	NaOH/Liver %	Pick up oil: Species of fish liver oil	Pick up oil: Vitamin A unit U.S.P.U.	Pick up oil: Quantity of addition kg.	Pick up oil: Ratio of added %	pH value	Heating temperature °C	Oil quantity kg.	Vitamin A unit U.S.P.U.	Vitamin D unit I.U.
Aug. 3, 1949	150.0	4.2	2.80	Codfish	—	10.0	6.6	9.4	80	6.0	—	—
Oct. 5, 1949	418.0	15.7	3.75	Halibut yellow tail codfish	10000	29.2	6.9	9.4	80	29.4	30790	15700
June 8, 1950	176.0	9.2	5.22	Codfish	12000	12.0	6.8	9.2	80	13.0	22600	9780
July 11, 1950	—	—	—	Shark	—	—	—	9.6	80	—	22300	16400

heating tank when livers had been completely decomposed and stirred for some 30 minutes at about 80°C.

III. Bonito Liver.

The same oil extraction method was applied to bonito livers as that which had been used for codfish livers. Tests were made with the help of pick-up oil.

METHOD OF EXTRACTION OF OIL.

Water used was about twice that of the raw material. The pH value of the material was adjusted to approximately 9.6 by adding NaOH solution of 20°–30° Bé. At 50°–60°C., when the condition of dissolution and separation was good, 7% of pick-up oil was added. Then the pH was readjusted. About one hour later, temperature of material was raised and maintained at 80°–85°C., at which temperature it was stirred for nearly one hour. Water was led in to allow it to be skimmed easily. At 50°–60°C., stopped the stirring. Covered it until the next morning when the upper layer was skimmed and centrifuged to obtain crude oil.

RESULTS:–

Results were shown in Table III.

In this case the quantity of NaOH used was higher than that used for livers of the other fishes. Bonito liver has a very small oil content itself and its oil extraction without the help of pick-up oil is nearly impossible. The vitamin A unit and vitamin D unit values of bonito liver oil are 11,000-20,000 U.S.-P.U. and 10,000-16,000 I.U. respectively.

Summary

(1) On extracting liver oil from codfish liver alone and codfish whole internal it is good to operate at pH 8.0. At this pH value rate of oil extraction is 20–30% and the vitamin A unit about 10,000 U.S.P.U.

(2) The optimum pH for the oil extraction of shark liver is 9.0–10.0. Oil rate is 40–50%. The vitamin A unit values of both great blue shark and salmon shark are ca. 3,000 U.S.P.U. while that of dogfish black liver is very large reaching to about 40,000 U.S.P.U. which is about twice of the white color liver form the same kind of shark.

(3) The oil extraction of bonito livers must be performed with the help of pick-up oil. Its vitamin A unit is 10,000–20,000 U.S.P.U. It contains a large quantity of vitamin D too.

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海洋底質の化學的研究

第 5 報　海底土による海水溶存酸素の消費作用について

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CHEMICAL STUDIES ON MARINE DEPOSITS

V. ON THE CONSUMPTION OF WATER-DISSOLVED OXYGEN BY BOTTOM DEPOSITS.

Taizo OKUDA and Kenji KATO

In sea bottom, the deposits consume the oxygen dissolved in sea water. As to the qualities which seem to have influence on the oxygen consumption by the deposits, one may indicate various factors, as biologicals or minerals. For the purpose of clarification of these factors, bottom samples taken from Onagawa-and Shiogama-Bay and from the sea to the northwest of Hokkaido Island were employed as experimental material in these investigations.

Pervious to the investigations, the effects of the experimental methods upon the oxygen consumption were examined individually with every experimental manner.

From the investigations the following results were obtained:

(1) The consumption velocity was adapted to the first reaction formula; elevation of temperature increased the consumptive action.

(2) The characters of bottom samples might influence the oxygen consumption, so these relations were investigated with mud of Shiogama-Bay; the results may be stated as follows:

(a) It seemed that the greater part of the oxygen consumption was not brought about by the biotic factors themselves, such as bacteria and enzymes, so much as by the reductive abiotic states caused by the former.

(b) The oxygen consumption by these reductive substances seemed to have some correlation with the carbon content of humus colloid and the particle radius of mud ($<10\mu$), but it was hardly possible to detect any correlation to the total sulfide content in mud.

(3) As to the bottom samples from the deep sea to the northwest of Hokkaido Island, it seemed that the consumption had negative correlation to the water depth of the site of deposition; it was difficult to detect any correlation with the organic carbon content of the deposit.

I. 緒　　論

海水中に溶存する化學成分は、そこに棲息する生物と密接な關連を有し、更にこれらは海底沈澱物

との間に一連の物質循環系をなしていることが知られており、従つて海底沈澱物は海洋の生產力に大きな役割を果している。

海水溶存酸素は海水中における酸化作用の主因をなすものであるが、大洋では概して水塊の流動が活潑で、湖沼のように環境の變化により、溶存酸素が減少して棲息する動物の呼吸作用に支障を來たすことは殆ど見られないようである。

しかし內灣などの樣に、有機物を始め種々の還元性物質の沈積の多い水域では、夏期停滯期において、その深層水中の酸素が著しく減少する場合がある。このことについては、深層水えの酸素の供給が不充分であること、植物の同化作用が表層に比して活潑でないため酸素の生產が少いこと、其他底棲生物による酸素の消費などが考えられるが、更に海底土中の還元性物質の酸化や海底細菌による消費など、所謂海底土による溶存酸素の消費も決して少くないものと思われる。

こゝに於て、近時環境要因としての水底土の研究が活潑となり、水底土による水中溶存酸素の消費に關する研究も多くの人々によつてなされている。すなわち、湖沼沈澱物については宮地[1]、山本[2]により、海洋沈澱物については元田[3]、川村[4]及び加藤（威）・松平[5][6]により、また、干潟地の酸素吸收については倉茂・太田[7]によつて研究がなされている。

本報に於ては、武藏堆を中心とした水深100～1,000米の陸棚及び陸斜の比較的深い海底の沈積物と、塩釜、女川兩港の如き淺い內灣の底土とを對象として、海底土による海水溶存酸素の消費作用の意義及び要因について研究を行つた結果について報告する。

本研究の遂行に際し、終始御懇切なる御指導を賜つた東北海區水產研究所增殖部長谷田專治博士、東北大學女川實驗所に於ける實驗に當り種々御便宜を頂いた東北大學農學部教授今井丈夫博士並に同實驗所の諸氏に深謝する次第である。また、武藏堆周緣の海底土採取に當つては、元北海道大學水產學部練習船「おしよろ丸」船長櫻庭誠三教授並に北海道水產試驗場苫米地洋文技官の御協力を賜つたが、玆に深く謝意を表する。なお、本研究の費用の一部を文部省科學研究費に仰いだことを記して謝意を表する。

Table 1. Tabulated Data of Bottom Samples of the Sea to the northwest of Hokkaido Island

St. No.	Position Lat. N	Position Long. E	Depth (meters)	Texture of Deposit	Organic Carbon %	Total Nitrogen %	Oxygen Consumption c.c./g×100
17	43° 30′ 30″	140° 29′ 48″	680	M	2.61	0.34	8.1
21	43° 30′ 30″	139° 59′ 12″	616	MS. Gr	1.22	0.12	5.3
24	43° 37′ 18″	140° 15′ 30″	760	M	2.18	0.49	3.3
30	43° 34′ 30″	140° 55′ 30″	145	Gr. S	0.64	0.07	5.4
31	43° 39′ 30″	140° 56′ 0″	450	M	2.53	0.27	6.1
51	43° 50′ 12″	141° 16′ 0″	147	MS	1.97	0.15	17.3
54	43° 39′ 36″	140° 57′ 24″	395	M	2.46	0.25	10.1
95	44° 3′ 30″	139° 59′ 24″	950	M	2.04	0.63	3.1
97	44° 4′ 12″	140° 12′ 6″	690	M	2.36	0.25	6.4
138	44° 14′ 42″	141° 17′ 0″	90	MS	1.32	0.09	11.5
141	44° 19′ 54″	141° 5′ 36″	340	M	2.11	0.31	13.2
184	44° 33′ 42″	139° 31′ 18″	590	MS	1.25	0.15	7.2
189	44° 34′ 12″	140° 6′ 6″	320	MS	0.49	0.06	5.2
195	44° 34′ 18″	140° 51′ 30″	230	MS	0.72	0.09	11.0
245	44° 52′ 54″	140° 34′ 30″	360	MS	2.02	0.27	15.0
248	44° 53′ 24″	140° 53′ 6″	140	S	0.98	0.17	12.0
264	45° 4′ 24″	140° 1′ 30″	512	MS	1.41	0.21	8.0
269	45° 3′ 42″	140° 36′ 6″	365	M	1.89	0.21	10.5
298	45° 19′ 30″	140° 37′ 6″	468	M	2.32	0.21	6.4
306	45° 24′ 18″	140° 18′ 42″	450	M	2.17	0.18	12.6

II. 實 驗 試 料

1. 北部日本海武藏堆周邊の試料は既報[8][9][10]と同様、昭和24年夏季北部日本海深海魚田調査に際し、本學部練習船「おしよろ」丸（506屯）で採取したもので、實驗は採泥現場に於て、採泥直後行つた。その試料の性狀については第1表に示した通りである。

この海域は黒潮の終端と親潮の尖端とが交錯し、武藏堆、天賣燒尻兩島を含み複雑多岐な海底形態を有する半深海性の海域で第3報に於て述べた如く底質中の有機物の C, N, C/N なども相當變化に富んでいる。

2. 塩釜港の試料については、酸素消費量と底質の諸性狀との關連性を檢討するため、昭和26年4月採泥し實驗に供した。

この港の特徴としては、深く入り込んだ楔形をなし、全般的に極めて水深が淺く、しかも年々泥土が堆積し淺くなる傾向があり、ために浚渫が絶えず行われて底質の變動も著しいものゝようである。港内は荒天でも外洋からの波浪を直接受けることは殆どなく、風力による港内水の擾亂以外は、單に干滿差に基く港内外水の緩漫な交換がみられるだけで、港奥水は停滯し勝ちである。從つて港内水の汚染の度合も甚だ大きく、底質も殆ど泥で、有機質に富む微細泥が廣く分布している。同港に於ける試料の採取地點並に性狀については、それぞれ第1圖及び第2表に示した。

Fig 1. Stations of Observation in Shiogama Harbour.

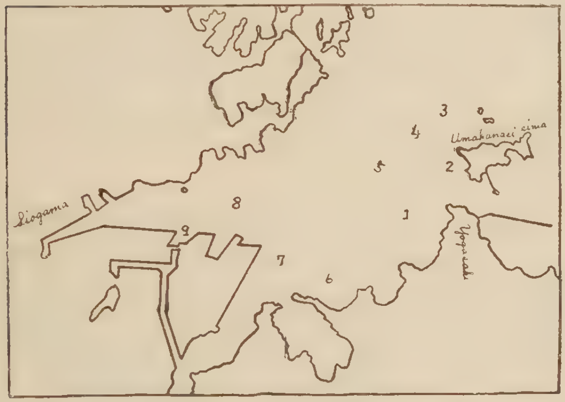


Table 2. Tabulated Data of Bottom Samples of Shiogama Harbour

St. No	Depth meters	Fine Mud <10μ %	Organic Carbon %	Total Sulphide %
1	1.5	67.4	2.60	0.055
2	1.8	79.1	2.92	0.127
3	2.0	47.3	1.95	0.001
4	1.5	73.5	2.92	0.115
5	1.0	62.4	2.79	0.109
6	1.2	78.4	3.42	0.163
7	7.0	89.5	3.21	0.284
8	4.5	88.2	3.08	0.668
9	3.0	40.3	4.15	1.174

3. 酸素消費量と作用溫度との關係につき實驗を行うに當り、東北大學女川實驗所の設備を使用させて頂いたが、その試料は同實驗所の沖合 500m, 水深 18.5m（試泥有機炭素量 2.76%）の地點より採取した。

III. 實 驗 方 法

1. 北部日本海武藏堆周邊の試料については採泥直後、船上で應急的に行つたもので、何分充分とは云い難い點も多いが、同海域の海底土の酸素消費作用の大要はうかがうことが出來たと信ずる。その方法としては、各採泥現場において 250c.c. 容の試藥瓶に 4c.c. の試泥をとり、基礎水として現場表面水を添加して空氣の殘らぬ様に密栓して上下に 50 回强振した後、12 時間靜置せしめた。しかる後、上澄液をサイフオンで靜かに酸素定量瓶に移し、殘存せる酸素をウインクラー法[14]によつて定量した。これより基礎水中の酸素量との差を求め、試泥（濕泥）100c.c. に對する酸素消費量を算出した。

2．塩釜港の試料については、採泥直後、現場で 1．の場合と同様、試薬瓶に試泥及び基礎水を加えた後、2 分間よく振盪し、24 時間靜置する。上澄液の酸素の定量は 1．と同様にして行つた。酸素消費量の算出にあたつては、試泥を乾燥秤量して、乾燥試泥 100g 當りの酸素消費量に換算した。

3．女川港の試料については、採泥後試泥は出來るだけ空氣との接觸をさける樣密栓して實驗所え持ち歸り、6c.c. の試泥をとり、種々の溫度の下で、同樣酸素の吸收を行わせた。酸素消費の測定を終つた試泥は濾紙上に移して乾燥秤量し、試泥の酸素消費量を乾燥泥 100g 當りに換算した。

Ⅳ．實驗の經過及び考察

A．實驗方法の予備的考察：—

底土による酸素消費作用に關して實驗する場合、その供試量、振盪法並に靜置時間などについては、それぞれ研究者により一定せずその方法も區々まちまちであるので、先づその實驗の方法について充分の檢討がなされねばならない。こゝにおいて著者等は本實驗に先立ち、その實驗方法に就いて次の如き二、三の基礎的な實驗を試みた。

以下(1)～(4)は塩釜港の試料につき、(5)は女川港の試料について行つた。

(1) 酸素消費量と試泥量

供試土の多少が酸素消費量に如何に影響するかを知るために、250c.c. の共栓瓶に種々の異つた量の試泥を加えて實驗した。その結果を第 3 表に示したが、供試土の量が多くなる程消費される酸素量が多くなるのは當然であるが、試泥單位量當りの酸素消費量は逆に著しく減少して來る。これは靜置した際沈澱し供試土の比表面積が減少するためではないかと思われる。從つて酸素の消費に關する比較を行うためには、一定量の試泥を採り實驗を行はねばならないものと考える。

Table 3. The Oxygen Consumption and the Quantity of Sample

Dried Sample (g)	0.53	0.93	2.13	3.79	9.98
O_2-Decrease (c.c./l)	2.02	2.13	2.81	3.84	4.94
Consumption c.c./g 100	81.0	48.7	27.2	20.3	10.0

Temperature 8.8°C

(2) 酸素消費量と採泥後實驗に供するまでの放置時間

嫌氣的な環境に置かれていた海底土を採取後、直ちに酸素消費力を測定した場合と、相當時間試泥を空氣中に放置した後に實驗に供した場合とでは、泥中の細菌の活動や空氣による酸化作用などのため、その酸素消費量が變つて來ることは當然予想されるところである。茲に於て採泥後、試泥を空氣中に、それぞれ 0, 6, 22, 30, 48 時間放置した後、その酸素消費力を測定したが、その結果は第 4 表の如くである。

Table 4. The Oxygen Consumption and the Exposed Time after Sampling

Time (h)	0	6	22	30	48
O_2-Decrease (cc l)	2.59	3.80	3.89	4.02	4.03
Consumption c.c./g × 100	24.8	30.1	31.7	33.3	32.5

Temperature 10.0 C

即ち採泥直後測定した場合の消費量は最低で、6 時間放置したものは急激にその酸素消費力を増大している。其後は放置時間を延長するも、その酸素消費量の増加は緩漫で略々一定の値に落付き著しい増加を認めることは出來なかつた。

(3) 酸素消費量と振盪時間

酸素の消費が比較的短時間内に相當活潑に進行することは、川村[4]及び倉茂・太田[5]も指摘しているが、著者等は試泥を基礎水に添加した後の振盪時間を種々に變えてその影響をしらべた。その結果

Table 5. The Oxygen Consumption and the shaken Time

Time (min)	2	4	6	10	20
O_2-Decrease(c.c./l)	2.77	3.05	3.00	3.35	3.31
Consumption c.c./g×100	32.0	35.0	36 1	38.1	42.6

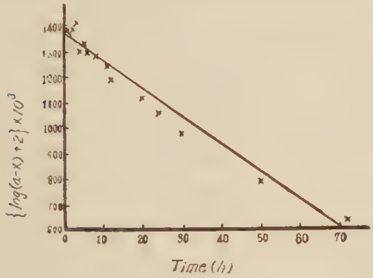
Temperature 8.8°C

は第5表に掲げたが、振盪時間が増すにつれて僅かに酸素消費量を増す傾向が見られた。なお、振盪は機械の準備がなかつたため、同一の速度を以て手で振盪した。

(4) 酸素消費量と作用時間

海底土による酸素消費の速度を吟味するため次の如き實験を行つた。即ち、予め恒溫槽中にて10°C (±0.1°) に保溫せる海水を基礎水として、同溫度において作用時間を變化して、その酸素消費量の變化を測定した。而してこの酸素消費が一次反應的に行われるものとすれば、作用後殘存している酸素量の對數はその作用時間に對して直線關係にあるべきである。

Fig 2. The Relation between the Oxygen Consumption and the Reacted Time. (Samples of Shiogama Harbour)



第2圖及び第6表は本實験における殘存酸素量の對數と作用時間との關係を示したものであるが、それらの間には直線的關係を認めることが出來る。

Table 6. The Oxygen Consumption and the Reacted Time

Temperature 10.0°C

Time (h)	a−x	{log(a−x)+2}×10³	Consumption c.c./g×100
0.5	0.242	1383.8	11.4
1.0	0.235	1371.1	11.6
2.0	0.244	1384.4	11.8
3.2	0.259	1413.3	14.4
4.0	0.200	1301.0	13.6
5.0	0.216	1334.5	15.7
6.0	0.203	1307.5	15.6
8.0	0.193	1285.6	17.4
11.0	0.175	1243.0	18.4
13.0	0.157	1195.9	20.4
20.0	0.133	1123.9	23.4
24.0	0.117	1068.2	23.6
30.0	0.097	986.8	25.1
50.0	0.063	799.3	29.4
72.0	0.044	643.5	32.2

a−x: Remained oxygen content after reaction c.c./g

即ち相關分析の結果は第8表に示した如く、0.1% 以下の危險率で直線性の有意なることが認められる〔$F_0=477.3>F'_{13}(0.001)$〕。而して海底土による酸素消費が一次反應的に進行することが確められた。

(5) 酸素消費量と作用溫度

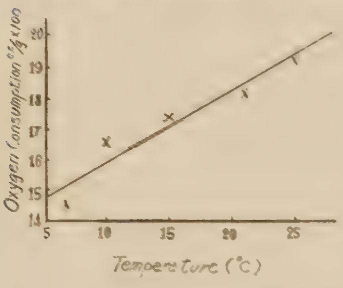
一般に化學反應速度は溫度の上昇と共に増加するが、女川港の底質を試料として、海底土の酸素消費量と溫度との關係をしらべた。即ち、予め田内式恒溫槽内で、それぞれ 6.8°C, 10.0°C, 15.0°C, の各溫度に保つた濾過海水を基礎水として、試泥を加えその溫度で24時間酸素の吸收を行わせた。その結果は第3圖及び第7表に示した通りであるが、それら酸素消費量と作用溫度との間には直線的關係があり、相關分析の結果に於ても、第8表に示した様に1% 以下の危險率で直線性の有意なることが確められた〔$F_0=174.1>F'_{13}(0.01)$〕。

なお、以上の予備實験に供した基礎水は、有機質少き外洋水を濾過して用いたが、更にこの海水中に含まれる細菌などによる酸素消費の程度を知るため空試験を試みたが、その影響は少くともこの實験においては殆ど無視してもよい程度であつた。

B. 酸素消費作用の要因と底質の諸性狀との關係:—

海底土の酸素消費の主因としては海底土中に生活する細菌などによる生物的要因や、腐植其の他の

Fig 3. The relation between the Oxygen Consumption and the reacted Temperature (Samples of Onagawa Harbour)



有機物や重金属其他の無機物質の如き化学的要因を予想出来るが、加藤（威）[6]はその主因を泥の腐敗分解に帰し、川村[4]は消費量が粒子組成の微細なものほど多いことを指摘している。更に倉茂・太田[5]は酸素消費に與る要因としては有機物、鐵塩及び硫化物等の無生物的要素が主で、細菌や酵素の様な生物的要素は割合に少いものであることを報告している。また、湖沼については、宮地[1]は湖沼の榮養化の程度と關係あることを推論し、山本[2]は富榮養湖においては明かに灼熱減量と正相關的な關係を示し、微生物や細菌との間には關係を認めることが出來なかつたと述べている。

Table 7. The Oxygen Consumption and the Temperature

Temperature (°C)	Sample (g)	Original (O_2c.c./l)	Decrease (O_2c.c./l)	Consumption c.c./g×100
6.8	4.81	5.45	3.39	14.6
10.0	4.20	5.36	3.33	16.6
15.0	4.28	5.30	3.60	17.4
21.0	4.42	5.18	4.14	18.2
25.0	4.19	4.86	4.06	19.3

斯くの如く海底土による酸素消費の要因については種々の論議があるが、著者等もその要因について検討するため、先ず底質の性状と酸素消費の關係について吟味した，即ち塩釜港の9地點より得た底質を試料とし、その酸素消費と底質中の有機物、硫化物、粒子組成との關係につき考察し、また泥中の細菌や酵素による影響を検討した。なお、それらの關係を示す分析の結果は第9表に纏めて掲げた。

Table 8. Analysis of Correlation Table

	(1) The relation between the oxygen consumption and the time (samples of Shiogama Harbour)				(2) The relation between the consumption and the temperature (samples of Onagawa Harbour)			
Factor	Variation	Degree of Freedom	Unbiased Estimator	F	Variation	Degree of Freedom	Unbiased Estimator	F
Regression	707.795	1	707.795	475.7	11.5	1	11.5	31.1
Residual	19.339	13	1.488		1.1	3	0.37	
Total	727.134	14			12.6	4		

まず、酸素消費の要因の大要をうかがうために、倉茂・太田[5]の行つたと同じ方法を用いて試泥を處理した。

(1) 細菌並に酵素による消費の検討：—

細菌並に酵素が酸素の消費に與る程度をしらべるために、それぞれ次の如く試泥を處理した。すなわち．

A. 採泥直後篩の上で自然状態のまゝで作用させた場合……全要素による消費

B. 採泥直後篩の上で試泥にトルオールを数滴添加し良く攪拌して、細菌の活動を停止させた後作用させた場合……細菌の作用が停止し、細菌による消費量だけAより減少

C. 沸騰水中に30分間試泥を浸漬し、細菌及び酵素の作用を停止せしめた後、冷却し實驗に供した場合……Aより細菌及び酵素の作用が減少

Table 9. Analysis of Correlation Tables (Samples of Shiogama Harbour)

(1) The relation between A※ and the organic carbon content in bottom deposit
(9 samples were used)

Factor	Variation	Degree of Freedom	Unbiased Estimator	F
Regression	14.9	1	14.9	1.61
Residual	168.0	7	24.0	
Total	182.9	8		

(2) The relation between A※ and the organic carbon content in bottom deposit
(8 samples were used)

Variation	Degree of Freedom	Unbiased Estimator	F
62.2	1	62.2	3.47
107.6	6	17.9	
169.8	7		

(3) The relation between C※ and the organic carbon content in bottom deposit
(9 samples were used)

Factor	Variation	Degree of Freedom	Unbiased Estimator	F
Regression	23.2	1	23.2	1.42
Residual	113.7	7	16.2	
Total	136.9	8		

(4) The relation between C※ and the organic carbon content in bottom deposit
(8 samples were used)

Variation	Degree of Freedom	Unbiased Estimator	F
89.9	1	89.1	13.75
38.9	6	6.48	
128.0	7		

(5) The relation between the organic carbon content and fine mud content
(9 samples were used)

Factor	Variation	Degree of Freedom	Unbiased Estimator	F
Regression	1.6	1	1.6	204.8
Residual	2,293.8	7	327.7	
Total	2,295.4	8		

(6) The relation between the organic carbon content and fine mud content
(8 samples were used)

Variation	Degree of Freedom	Unbiased Estimator	F
1,049.1	1	1,049.1	17.75
354.4	6	59.1	
1,403.5	7		

(7) The relation between C※ and the fine mud content
(9 samples were used)

Factor	Variation	Degree of Freedom	Unbiased Estimator	F
Regression	62.4	1	62.4	5.89
Residual	74.5	7	10.6	
Tatal	136.9	8		

※ A: The oxygen consumption measured on boat soon after sampling.

C: The oxygen consumption measured, after samples were soaked in the boiling water for half an hour for keeping without the actions of bacteria and enzymes.

これより

A—B＝　細菌のみによる酸素消費量

B—C＝　酵素のみによる酸素消費量

C＝　細菌や酵素以外（倉茂等の呼稱に倣つて無生物的要素と稱す）による酸素消費量

が算出される。

その結果は第10表に掲げた様に倉茂・太田の結果と大體一致する。即ち、細菌や酵素などの生物的要素による消費は少く、それら以外の無生物的要素による消費が最も大きいことが知られる。

なお、トルオール處理を行つた場合のトルオールによる酸素消費の影響を見るために空實驗を行つたが、トルオールによる消費は認められなかつた。

(2) 細菌及び酵素以外（無生物的）の要素による消費の検討：—

Table 10. Disscusion on the Causes of the Oxygen Consumption (Samples in Shiogama Harbour)

St. No.	A	B	C	A－B	B－C
1	39.7	34.1	23.4	5.6	10.7
2	31.9	31.8	23.5	0.1	8.3
3	28.9	22.7	16.0	6.2	6.7
4	32.9	31.7	23.2	1.2	8.5
5	42.1	34.0	23.2	8.1	10.8
6	41.5	38.9	30.2	2.6	8.7
7	37.8	36.4	22.0	1.4	14.4
8	40.2	39.2	28.5	1.0	10.7
9	33.5	32.4	20.6	1.1	11.8

A: Measured, on boat, soon after sampling (Consumption by all factors)
B: Measured, after the actions of bacteria of samples were stopped by adding toluol on boat (for keeping without the action of bacteria)
C: Measured, after samples were soaked in the boiling water for half an hour (for the purpose of keeping without the actions of bacteria and enzymes)
A—B: Consumption by bacteria only
B—C: Consumption by enzymes only

海底土による酸素消費の主因をなす無生物的要素による消費量につき検討するため、試泥の硫化物及び有機物の含有量並にその微粒泥量との關係について考察した。

(a) 酸素消費と硫化物との關係

硫化物の定量は富山・神崎[11]の方法により行つた。即ち、供試湿泥をミクロ窒素蒸溜装置を用い、10% HClを2c.c.加えて5～8分間蒸溜を行い、蒸溜液を5c.c.の飽和醋酸亜鉛溶液中に捕集する。生成した硫化亜鉛に一定量の沃度液及び10%HCl 2c.c.を加えて酸化し、殘存せる沃度を$Na_2S_2O_3$標準液で滴定し、その消費沃度量より硫化物量を算出し、乾泥1kg當りの含有量に換算した。その結果は第4圖に示してあるが、硫化物含量と酸素消費量との間には相關性を認めることは出來なかつた。

(b) 酸素消費と微粒泥量との關係

A. S. K. 式土壌淘汰分析装置[12]によつて10μ以下の微細泥量を求めたが、その量と酸素消費量との間には第5圖の如く正の相關性を認めることが出來た。相關分析の結果は第9表(7)の如くで、5%以下の危險率で直線性が有意であることが確められた〔$F_0=5.89>F'_7(0.05)$〕。

(c) 酸素消費と有機炭素量との關係(第6, 7, 8圖)

試泥中の有機炭素の定量は既報と同様、Tyulin[13]の簡易滴定法に依り行つた。

塩釜港の試料について、有機炭素量と、採泥直後自然狀態のまゝで作用させた全要素による酸素消費量との關係について、その直線性に關して相關分析を行つたが、それらの間には相關があるとは云えない結果を得た〔$F_0=1.97<F'_7(0.05)$〕。しかし、これら塩釜港の9個の試料のうち、No. 9の試料は岸壁に近い港奥の船舶が停泊する水域より得たもので、そのなかには未分解の有機質の碎片を數多混有し、其他の地點に

Fig 4. The Relation between the Oxygen Consumption and the Total Sulphide Content. (Samples in Shiogama Harbour)

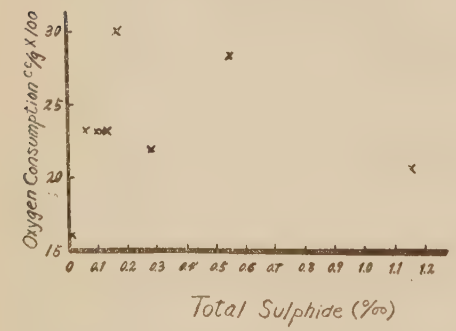


Fig 5. The Relation between the Oxygen Consumption and the Fine Mud (Samples of Shiogama Harbour)

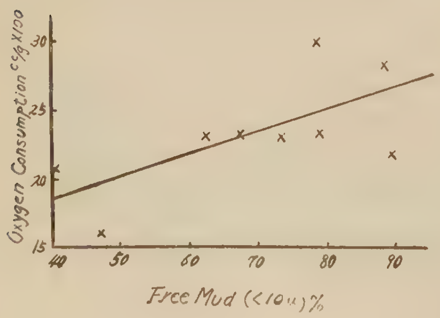


Fig 6. The Relation between the Oxygen Consumption and the Organic Carbon Content (Samples of Shiogama Harbour)



Fig 7. The Relation between the Oxygen Consumption and the Organic Carbon Content (Samples of Shiogama Harbour)

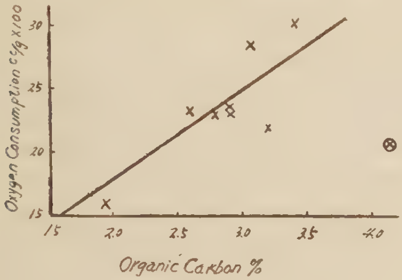
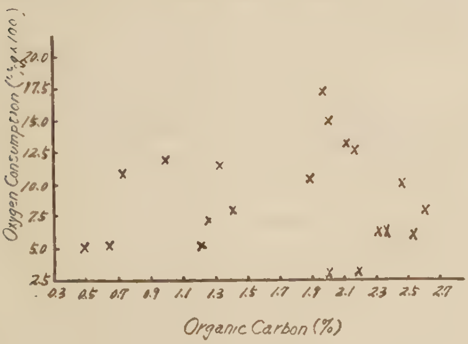


Fig 8. The Relation between the Oxygen Consumption and the Organic Carbon Content (Samples of the sea to the northwrest of Hokkaido island)



比べて明かに特異な性狀を呈していた。而して、この地點を除外した他の8地點の試料について、有機炭素量との關係について、その直線性の相關分析を試みたが、やはり、その有意性を認めることが出來なかつた。從つて試料數の少數なことにもよるのであろうが、それらの間には相關性があるとは云えないのではなかろうか〔$F_0=4.24<F'_6(0.05)$〕。即ち自然狀態で作用させた（全要素による）酸素消費量は、有機炭素量と關係があるとは云えず、從つて海底土による酸素消費の大部分が必ずしも有機炭素に基くものと考えられない。

この問題に關して、更に吟味するために次の樣な考察を試みた。

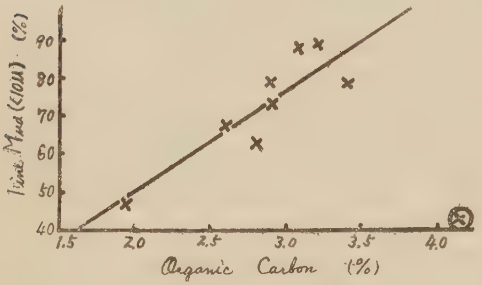
いま、試泥を煮沸處理して作用させた無生物的要素による酸素消費量と試泥の有機炭素量との關係につき檢討し、相關分析を試みた。しかしその結果からもその直線性の有意性を認めることが出來なかつた。そこで、著者等は第7圖に丸印を附した前出の特異地點（No. 9）の試料の吟味を行い、1% 以下の危險率を以て棄却されることを確め、この値を棄却した殘りの8個の試料について、更に酸素消費量と有機炭素量との相關性に關して相關分析を行つた結果、その有意性を確めることが出來た。（$F_0=11.95>F'_6(0.01)$）從つて細菌及び酵素以外の無生物的要素による酸素消費は少くとも有機炭素量と相關性のある樣に思われる。

しかるに一方、武藏堆周邊の底土について、その酸素消費量と有機炭素含量との關係について檢討して見たが、第8圖に示した如く相關性を認めることは出來なかつた。これは、この海域が淺海性及び半深海性を含む複雜な海底形態を有するため、その海底土中に含まれる有機物もその性質や形態の異つた種々の物質より成立つているため、有機物量と酸素消費量との相關を求めても、不規則な結果が得られたものと思われるが、この點に關してはこれを明かにすることは出來なかつた。

d）微粒泥量と有機炭素量との關係

塩釜港の試泥についてA. S. K. 式淘汰器によつて定量した10μ以下の微粒泥の量と、有機炭素含量との關係については第9圖に示した通りであるが、その相關の直線性の檢定を行つた結果、その有意性を認めることは出來なかつた〔$F_0=205<F'_7(0.05)$〕。そこで、前出の特異地點No. 9について棄却

Fig 9. The Relation between the Fine Mud and Organic Carbon Content.
(Samples of Shiogama Harbour)



検定を試みた結果、1% 以下の危険率を以て棄却し得ることを確めたので〔$F_0=34.05>F'_6(0.01)$〕、残りの 8 地點の試料について再び相關分析を行つた結果、1% 以下の危険率を以て、試泥の微粒泥量と有機炭素量との間には正相關があることが判つた〔$F_0=17.75>F'_6(0.01)$〕。

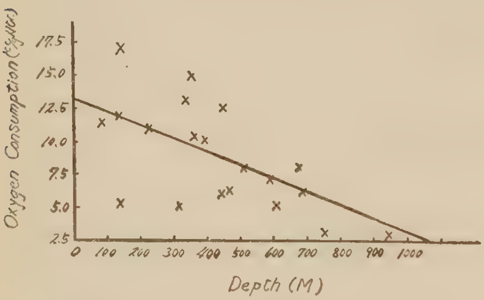
以上無生物的要素殊に有機質による酸素消費に關する考察を總括すると次の如く要約することが出來るであろう。即ち.

海底土による酸素消費の主因をなすものは、細菌や酵素の様な生物的要素ではなく、寧ろ化學的な無生物的要素であつて、しかも含有有機質が相當大きな役割を果している。しかし、海底土中に含まれる有機物と云つても、簡單にあらゆる形態の有機物と關係がある譯ではなく、微泥粒量と有機炭素量の相關性や棄却値の吟味などより、海底に於て相當分解をうけ、微粒化し、所謂腐植膠質と稱せられる狀態になつた有機質が主要な役割をなしていると考えるべきであろう。

(3) 深海底土の酸素消費量と水深との關係：—

武藏堆周邊の底土について、その酸素消費量と水深との關係を吟味したが、その結果は第 10 圖及び第 11 表に示した如く、酸素消費量と水深との間には負の相關性が存在し、水深を増すと共に酸素消費量が減少する傾向が認められた〔$F_0=12.66>F'_{18}(0.01)$〕。

Fig 10. The Relation between the Oxygen Consumption and the Water Depth
(Samples of the sea to the northwest of Hokkaido Island)

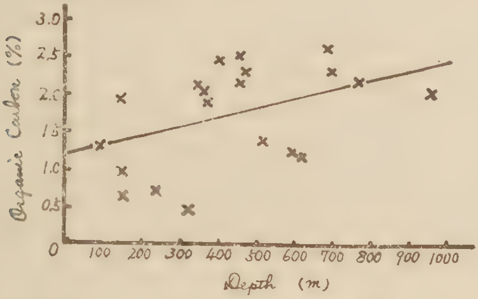


しかるに一方、水深と有機炭素量との間には第11圖に示した如く（詳細は第3報參照）、正の相關が認められ〔$F_0=4.69>F'_{18}(0.01)$〕、水深と共に炭素量は増加している。而して、この様な酸素消費量と水深及び有機炭素量との關係は一見甚だ矛盾している様に見えるが、これは前項に於て酸素消費と有機炭素量との關係を論じた際にも觸れた様に、むしろ複雑な海底形態を有する亞洋性底質の特異性とも考えるべきもので、Waksmann[15] が、淺海性堆積物と深海性堆積物とでは、細菌による底質有機物の酸化分解過程が同一ではなく、深海性堆積物中の

Table 11. Analysis of Correlation Table
(Samples of the sea to the northwest of Hokkaido Island)

	(1) The relation between the oxygen consumption and the depth of water.				(2) The relation between the organic carbon content and the depth of water.			
Factor	Variation	Degree of Freedom	Unbiased Estimator	F	Variation	Degree of Freedom	Unbiased Estimator	F
Regression	110.9	1	110.9	11.27	1.83	1	1.83	4.69
Residual	177.1	18	9.84		7.09	18	0.39	
Total	288.0	19			8.92	19		

Fig 11. The Relation between the Organic Carbon Content and the Water Depth (Samples of the sea to the northwest of Hokkaido Island)



有機物は極めて抵抗性の強い海底腐植となつているため酸化分解され難いことを指摘していることゝ併せ考えれば甚だ興味深いものがある。

塩釜港の場合は、極めて水深が淺く、しかも水深に變化が少いため、水深の差による海底土の酸素消費量の差違を比較することは出來なかつた。

以上の實驗結果を總括するに、海底土による酸素消費の原因となるべき要素は決して單純なものではなく、複雜且つ有機的關係を有する總合的要素によることが明かであるが、そのうち有機質其他を主體とする無生物的或は化學的要素が最も主要な要素の樣に思われる。しかし、それらについても海底形態や海況の如き環境要因による影響をも含め、泥中の細菌や微生物の生活活動と關連して充分の考察がなされねばならないであろう。

V. 摘　　要

1. 環境要因としての海底土による海水溶存酸素の消費作用を檢討するに先立ち塩釜港及び女川港の底土を試料として、實驗方法、即ち供試土の量、振盪時間、實驗に供するまでの放置時間、作用時間、並に作用溫度などについて予備的實驗を試みた。

2. 而して海底土による酸素消費の進行が一次反應式に適合することを確め、更にその消費量は作用溫度の上昇と共に增加することを明かにした。

3. 塩釜港の試料について、酸素消費量と底質の諸性狀との關係につき檢討し、酸素消費の要因について考察を加えた。

(1) 海底土による酸素消費の主因をなすものは細菌や酵素の樣な生物的要素ではなくて、むしろ化學的、或は無生物的要素であろうと思われる。

(2) この酸素消費の主因をなす無生物的要素による消費作用は、この場合では硫化物含量との關連性を認めることは出來ないが、有機質殊に海底に於て相當分解過程の進行した腐植膠質的形態のものと相關關係をもつている樣に見える。

4. 武藏堆を中心とした半深海性の海底土の酸素消費量は、水深とは負相關的であり、且つ有機炭素量とも相關性が認められないなど、亞洋性海域の興味ある特異性を示している。

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(水產科學研究所業績　第 95 號)

海藻に關する化學的研究

第 4 報　含硫黄アミノ酸の檢索

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CHEMICAL STUDIES ON MARINE ALGAE

IV. ON THE AMINO ACIDS CONTAINING SULPHUR.

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Y. Oishi has separated dimethyl sulphide as a flavouring matter from marine green algae. he concluded that it was produced from the algae by the action of some peculiar bacteria.

The present authors have studied the kinds of amino acids containing sulphur which are obtained from various species of marine algae, in order to ascertain whether the methyl mercaptane as the source of dimethyl sulphide may be produced from methionine or cystine in the algae. The method by Winegard, Toennis and Block was employed.

The experimental results are as follows:

(1) The presence of hydrolyzate of cystine was recognized in all marine algae. The quantity of the hydrolyzate of cystine is largest in marine brown algae, next in green algae and least in red algae.

(2) No methionine could be detected in any of the marine algae.

緒　　言

海藻中の含硫黄アミノ酸については田所、宇賀神[1]両氏及び奥山[2]氏が褐藻、緑藻、紅藻に於けるシスチンの分布を研究し、シスチン含量は一般に褐藻に多く、緑藻、紅藻の順に減少することを認めている。

一方 A. Mazur & H. T. Clarke[3] 両氏は *Phormidium*, *Ulva*, *Laminaria*, *Sargassum*, *Chondrus*, *Osmunda* につき、その系統發生の順位と含硫黄アミノ酸との關係を調べ、これらの中最下等なる水生植物、*Phormidium* に於てはメチオニンを含有するがシスチンを欠除し、次に位する海藻、*Ulva* (緑藻)、*Laminaria*, *Sargassum* (褐藻)、*Chondrus* (紅藻) に於てはシスチンを含有するがメチオニンを欠除している。然し更に高等なる *Osmunda* に到つて始めてシスチン、メチオニンを併せ含有すると云う興味ある報告がある。

大石[4]、五十嵐、坂野[5]氏等は緑藻類の香氣成分としてヂメチル・サルフアイド ($CH_3\text{-}S\text{-}CH_3$) を分離し、これが藻體より微生物の作用によつて二次的に生ずるものであるとした。更に同氏等はその生成機構に關し藻體中に存在するスルフオン酸メチル・エステル ($CH_3O\text{-}SO_2OR$) が微生物の作用で藻體より生じたメチル・メルカプタン (CH_3SH) と反應してヂメチル・サルフアイドを生ずるもの

であろうと推論し、メチル・メルカプタンを生じ易い含硫黄化合物の存在を想定している。

一方鬼武[5]氏は含硫黄アミノ酸より微生物によるメチル・メルカプタンの生成機構を研究し、システチンよりはグルコース、ラクトース又はヒスチヂンの共存に於てのみ生ずるが、メチオニンよりは以上の存在せざる時に於ても生成されると述べている。

著者等はヂメチル・サルフアイド生成因としてのメチル・メルカプタンが何れの含硫黄アミノ酸に基因するかを確めるために最近 Winegard, G Toennis & R. J. Block[6] 氏等によつて行われた處の含硫黄アミノ酸のペーパー・クロマトグラフ法に從い、海藻中の含硫黄アミノ酸の檢出を行い茲に得られた結果を報告して參考に供するものである。

實驗試料並びに實驗方法

實 驗 試 料：—

函館市外七重濱にて採取せる極めて新鮮なる藻體を水洗し、後速かに風乾し更にこれを 80°C の乾燥器中にて乾燥したる後粉末として實驗に供した。又ナルトワカメは市販品を用いた。

實 驗 方 法：—

1．**鹽酸加水分解物.** — 試料約 50mg をとり 10c.c. の 8N–HCl と共に封管中で 105°～110°C に 24 時間加熱加水分解したる後時計皿上に滌ぎ出し、湯浴上で濃縮乾固を反復して可及的に HCl を追い出す。

2．**ペーパー・クロマトグラフ法.** — 2cm×40cm の濾紙（東洋濾紙 No. 2）を用い、溶媒滲透端より 7cm 距てた點にアミノ酸として 0.1mg 内外に相當する量の加水分解液を約 2cm の範圍につけ、乾燥後フエノール（10% の水を添加）又はブタノール（95% 水飽和）を入れた淺い平皿上にその一端を浸し、上昇法により溶媒を毛細管現象で約 30cm の高さ迄滲透せしめる（密閉容器中 20°C, 約 18 時間を要す）。次いで溶媒を加溫蒸發せしめた後アセトン、エーテル 1:1 の混液で洗い、クロマトグラムに用いた溶媒を充分除去し 90°C で乾燥する。次いで 0.066N–KI 溶液と 0.0033N H_2PtCl_6 溶液の等量混合液をクロマトグラム上に噴霧するとクロマトグラムは桃色に染まるが、含硫黄アミノ酸の吸着されている部分は漂白されて白い Spot となることによりその存在を認めることが出來る。

實驗結果並びに考察

第 1 表は標準となるべき含硫黄アミノ酸のフエノール及びブタノールに對する Rf–値を求めたものである。

Table 1. Rf–Value on Paper Chromatogram of Amino Acids Containing Sulphur.

Amino Acids	Rf–Value		Bleaching time
	Phenol	Butanol	
Cystine	0.053～0.066	0.011～0.013	1 min.
Methionine	0.695	0.571	immediate

次に第 2 表は各種海藻につき含硫黄アミノ酸の存在を檢索したる實驗結果を示せるものである。

以上の實驗に於て紅藻類中アカバ、イトグサ、ダルスはフエノールを溶媒とせる時シスチンの反應は檢出せられず、且クロバギンナンソウ及びボーアヲノリに於てもその存在は痕跡程度であつた。然しブタノールを溶媒とせる時は明らかにシスチンの存在による脫色反應が認められた。而るに何れの海藻に於てもメチオニンは檢出し得られなかつた。即ち海藻中

Table 2. Rf–Value on Paper Chromatogram of Amino Acids Containing Sulphur Obtained from Various Species of Marine Algae

	Species		Phenol				Butanol			
			Cystine	Rf–Value	Methionine	Rf–Value	Cystine	Rf–Value	Methionine	Rf–Value
Brown Algae	MAKONBU	*Laminaria japonica* ARESCH.	卄	0.055	—	—	卄	0.013	—	—
	NANBUWAKAME	*Undaria pinnatifida f. distans* MIYABE et OKAM.	卄	0.052	—	—	卄	0.013	—	—
	AINUWAKAME	*Alaria crassifolia* KJELLMAN	卄	0.050	—	—	卄	0.010	—	—
	NARUTOWAKAME	*Undaria pinnatifida f. narutensis* YENDO	卄	0.052	—	—	卄	0.011	—	—
	KAYAMONORI	*Scytosiphon Lomentaria* (Lyngb.) J. AG.	卄	0.052	—	—	卄	0.013	—	—
	FUKURONORI	*Colpomenia sinuosa* DERB. et SOL.	卄	0.053	—	—	卄	0.011	—	—
Green Algae	AOSA	*Ulva pertusa* KJELLMAN	卄	0.053	—	—	卄	0.013	—	—
	AONORI	*Enteromorpha Linza* (L.) J. AG.	卄	0.064	—	—	卄	0.019	—	—
	USUBAAONORI	*Enteromorpha Linza* var. *crispata* J. AG	卄	0.053	—	—	卄	0.017	—	—
	BŌAONORI	*Enteromorpha intestinalis* (L.) LINK	±	—	—	—	+	0.014	—	—
Red Algae	ASAKUSANORI	*Porphyra tenera* KJELLMAN	+	0.048	—	—	+	0.010	—	—
	UPPURUINORI	*Porphyra pseudolinearis* UEDA	+	0.060	—	—	+	0.010	—	—
	CHISIMAKURONORI	*Porphyra umbilicalis* (L.) J. AG.	+	0.053	—	—	+	0.010	—	—
	KURONORI	*Porphyra Okamurai* UEDA	+	0.053	—	—	+	0.013	—	—
	TSUKUSIAMANORI	*Porphyra crispata* KJELLMAN	卄	0.053	—	—	+	0.011	—	—
	MARUBAAMANORI	*Porphyra suborbiculata* KJELLMAN	+	0.053	—	—	+	0.013	—	
	AKABA	*Neodilsea Yendoana* TOKIDA	—	—	—	—	+	0.013	—	—
	TSUNOMATA	*Chondrus ocellatus* HOLMES	+	0.052	—	—	+	0.010	—	—
	TOGETSUNOMATA	*Chondrus armatus* (HARV.) OKAM.	+	0.050	—	—	+	0.011	—	—
	ITOGUSA	*Polysiphonia* sp.	—	—	—	—	+	0.011	—	—
	KUROBAGINNANSO	*Iridophycus laminarioides* (BORY) SET. et. GARDN.	±	—	—	—	+	0.014	—	—
	DARUSU	*Rhodymenia palmata* (L.) GREV.	—	—	—	—	+	0.014	—	—
	NUMEHANORI	*Delesseria violacea* (HARV.) KYLIN	+	0.053	—	—	+	0.011	—	—
	HIRAMUKADE	*Grateloupia livida* (HARV.) YAMADA	+	0.057	—	—	+	0.013	—	—
	MUKADENORI	*Grateloupia filicina* (WULF.) AG.	+	0.053	—	—	+	0.013	—	—
	FUSITSUNAGI	*Lomentaria catenata* HARV.	+	0.050	—	—	+	0.013	—	—
	EZOTOSAKA	*Erythrophyllum Gmelini* (GRUN.) YENDO	+	0.053	—	—	+	0.013	—	—
	YUNA	*Chondria crassicaulis* HARV.	+	0.053	—	—	卄	0.013	—	—

にはその種類を問わず含硫黄アミノ酸としてシスチンの存在することが判る。而もその含有量を脱色反應の強弱より判斷すると田所、宇賀神兩氏及び奥山氏が指摘せる如く一般に褐藻に多く綠藻、紅藻の順に減少することを認めた。

著者等は別に多數の海藻中に遊離のヒスチヂンの存在することを認めたのでヂメチル・サルフアイド生成因としてのメチル・メルカプタンは海藻中に廣く存在する遊離のヒスチヂンの共存の下でシスチンより二次的に生ずるものではなかろうかと推論される。

要　　　約

1．各種海藻中には含硫黄アミノ酸としてシスチンを含有している。而してその含有量は一般に褐藻が多く綠藻、紅藻の順に減少する。

2．各種海藻中には含硫黄アミノ酸としてメチオニンを含有していない。

終りに臨み終始御懇切な御指導と御鞭撻とを賜わりし本學部教授農學博士、醫學博士村田喜一先生に深甚なる謝意を表する次第である。

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（水產科學研究所業績　第96號）

海藻に關する化學的研究

第 5 報　アマノリ中の有機塩基について

高　木　光　造　（水産食品化學教室）

CHEMICAL STUDIES ON MARINE ALGAE.

V. ORGANIC BASES IN *Porphyra pseudolinearis.*

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The author has tried to separate systematically the organic bases which are present freely in *Porphyra pseudolinearis*, and obtained the following results.

(1) Adenine, histidine and lysine were separated as picrates. Arginine and choline could not be separated, but they are perhaps present in it.

(2) The general distribution of nitrogen in *Porphyra pseudolinearis* was ascertained.

緒　　言

海藻中にトリメチルアミンの如き揮發性の塩基が存在する事については既に Klebahn[1]、Haas & Hill[2]、Kapeller-Adler & Csato[3]、白濱[4]氏等によつて知られている處であるが、尙この他にも不揮發性の塩基として戸田[5]氏は *Porphyra umbilicalis* 中にスタキドリンの存在を、Zeller[6] 氏は 10 種の海藻につきコリンの存在を、荻野[7][8]氏は *Laminaria sp.* 中にスタキドリン、コリン及びアデニンの存在を確認しグアニン、キサンチンの存在を推定している。同氏[8]は又 *Sargassum Ringgoldianum* 中にヒスチヂン、コリンの存在を確認し、トリゴネリン及びリジンと思われる結晶を分離した。

著者は前にアマノリ加水分解液中のアミノ酸をペーパー・クロマトグラフ法によつて求めた結果、未知の Spot の存在を認めたのでこれの分離確認を攻究すると共にアマノリ中の有機塩基について系統的分離を試みる必要を感じこの實驗を企圖した次第である。玆に得られた結果を報告して參考に供するものである。

實　驗　結　果

〔1〕 ウツプルイノリ (*Porhyra pseudolinearis*) の熱湯抽出エキスの調製.

ウツプルイノリは北海道福山產の市販品で採取時期は所謂寒ノリと稱せられる 1 月から 2 月の期間である。

ウツプルイノリ市販品 500g を用い細切せる後熱湯 8L を加え湯浴中にて 70°～80°C で約 2時間攪拌しつゝ抽出を行う。更にこの操作を 2 回繰返す。次いで綿布にて濾過し濾液約 21L を得た。その全窒素は 6.82g にして試料 500g 中の全窒素 29.05g に對し 23.8% に相當した。この際殘渣 3.4kg を得た。

次に塩基性醋酸鉛 400g を 1.5L に溶解せし液を加えて溶解蛋白を充分沈澱せしめ、これを濾別し濾

液22.5Lと殘渣約900gを得た。而して濾液中の全窒素は3.36gにして500g中の全窒素に對し11.5%に相當し、ウツプルイノリ熱湯抽出液の全窒素に對し49.2%に相當した。次いでH_2Sにて過剰の鉛を除き減壓濃縮して全量を500c.c.にする。この時得られた濃縮液は黄褐色を呈する。

〔2〕 熱湯抽出液より塩基性成分の分離について.

熱湯抽出エキスにH_2SO_4を5%となる樣に加え、更に20%燐タングステン酸水溶液1Lを加えれば塩基性物質の沈澱生成は大體に於て完結する。これを一夜放置したる後遠心分離して沈澱を集む。沈澱量(未乾燥)は300g得られた。この沈澱を$Ba(OH)_2$飽和溶液にて分解し、常法により遊離塩基溶液として全量を250c.c.とした。かくして得られた遊離塩基溶液中の全窒素は0.736gにして熱湯抽出液の全窒素に對し10.7%に相當する。而して濾液即ち熱湯可溶非蛋白液中の非塩基性窒素の全量は2.424g、全液量は1.24Lであつた。

(1) プリン塩基の部

遊離塩基溶液にHNO_3を加えてpH 5とし、これに20%$AgNO_3$溶液100c.c.を加えて銀塩を生成させた。かくして得られた銀塩を濾別し、Conc. NH_4OHにて充分洗滌したる後10%H_2SO_4にて加温分解しH_2Sにて脫銀し、更に過剰のH_2SO_4は$Ba(OH)_2$にて除き液のpHを1.2程度としたる後NaOHにてpH 6附近に中和する。これを濃縮して約5c.c.程度にすればプリン塩基類は結晶として析出する。

a) アデニンの分離確認:—

プリン塩基の混合物から先ずグアニンを分離する目的でNH_4OH處理を行つたが(グアニンは不溶)この際不溶物は殆ど得られなかつた。次にNH_3を減壓下に驅逐し、再び粗結晶となし、dil. H_2SO_4にて微酸性となし(液量20c.c.)温時ピクリン酸1gを加えて放置すれば長針狀のピクレートを析出する。結晶量0.392g, m. p. 275°C これを水より再結晶すればm. p. 281°Cを示し、アデニンモノピクレートに一致する。

分析結果は下記の樣でアデニンと確認した。

分 析:N 29.10%

$C_5H_5N_5 \cdot C_6H_3N_3O_7 + H_2O$としての計算値 N: 29.38%

アデニンピクレート分離母液を漸次濃縮したが他のプリン塩基を得る事が出來なかつた。

(2) ヒスチヂンの部

プリン塩基類の銀塩を分離した母液(全窒素量は0.370g)を$Ba(OH)_2$飽和溶液にて中和してpH 7程度とした時生成せる銀塩を濾別分離する。これよりH_2SO_4及びH_2Sにてバリウム及び銀を除去し、更に過剰のH_2SO_4は$Ba(OH)_2$にて除きpHを1.2程度としたる後NaOHにてpH 6附近に中和する。これについてヂアゾ反應を行つた所陽性でヒスチヂンの存在を示した。依つて更にこれを濃縮して約20c.c.としピクリン酸のアルコール溶液を加えて放置すれば黄色板狀のピクレートを析出する。結晶量0.307g、これを熱湯より再結晶すればm. p. 86°Cを示しヒスチヂン・ヂピクレートに一致する。冷水には稍々溶解し難し。

分析結果は下記の樣でヒスチヂンと確認した。

分 析:N 20.31%

$C_6H_9O_2N_3 \cdot (C_6H_3N_3O_7)_2$としての計算値 N: 20.55%

(3) アルギニンの部

ヒスチヂンの分離母液(全窒素量は0.307g)に更に$Ba(OH)_2$飽和溶液約100c.c.を加えてpHを9.6以上とした時生成せる銀塩を濾別分離し、これよりフラビアネートに導かんとせしも結晶を得ること

が出来なかつた。

(4) リジン塩基の部

アルギニン銀塩を濾別した濾液（全窒素量は0.260g）はdil. H_2SO_4にて過剰に存在する$Ba(OH)_2$を除き、H_2Sにて銀を除去して得た清澄な濾液を濃縮しH_2SO_4を5%となる様加えて更に20%燐タングステン酸溶液100 c.c.を添加し、一夜放置後沈澱を濾別する。黒褐色沈澱量約25g得られた。次に常法の如く処理して遊離塩基溶液を得、これにHClを加えて濃縮しデシケーター中にて乾固し、冷無水アルコール、熱アルコール、メチルアルコールにて浸出し3区分に分離した。

a) 冷無水アルコール可溶部

アルコールを蒸発し去りその少量の残留物に昇汞アルコール飽和溶液を加えて生じた沈澱を分離する。次いでこの沈澱物を水中に分散しH_2Sにて水銀を除き、H_2Sを駆逐したる後HCl塩に導き、これを真空デシケーター中に放置して吸湿性の結晶を得たるも極めて少量なりしためコリンの存在を確認することは出来なかつた。

昇汞沈澱を分離する母液は黄褐色を呈す。これを更にH_2Sにて水銀を除き濃縮し、これに塩化金のアルコール溶液を加えて塩化金複塩に導かんとせしも極めて少量なりしためスタキドリンの分離確認は出来なかつた。

b) 熱無水アルコール可溶部

アルコールを蒸発し去り、ピクレートに導かんとせしもこの部分は極めて少量のため結晶の分離確認は出来なかつた。

c) メチルアルコール可溶部

アルコールを蒸発し去りピクリン酸のアルコール溶液を加えて黄色針状結晶のピクレートを得た。結晶量0.103g, m. p. 251°C を示し、リジンモノピクレートに一致する。

分析結果は下記の様でリジンと確認した。

分　析：N 18.40

$C_6H_{14}N_2O_2 \cdot C_6H_3N_3O_7$ としての計算値 N : 18.67%

(5) トリメチルアミン

これは塩基を含有する燐タングステートを$Ba(OH)_2$にて分解する場合に蒸溜液中に捕収される。これはアルカリにて特有なる魚臭を発し、少量のHClを含む沃度加里液にて沈澱を生じ、又塩化金液によつて褐色の沈澱を生ずることによつてその存在を定性的に確認した。

第1表は以上の結果を従来の結果と比較表示したものである。

Table. 1 Comparison of the Results of Studies on Organic Bases in *Porphyra* by the Author and by Toda.

Author's result (*Porphyra pseudolinearis* 500g)				Toda's result (*Porphyra umbilicalis* 2kg)			
confirmed material	molecular formula	forms caught	yield (g)	confirmed material	molecular formula	forms caught	yield (g)
Adenine	$C_5H_5N_5$	picrat	0.392	Stachydrine	$C_7H_{13}NO_2$	chloraurat	no description
Histidine	$C_6H_9O_2N_3$	picrat	0.307				
Lysine	$C_6H_{14}N_2O_2$	picrat	0.103				
Trimethyl amine	C_3H_9N	Detected qualitatively					

第1圖は分確確認せるピクラートの顯微鏡寫眞を示したものである。

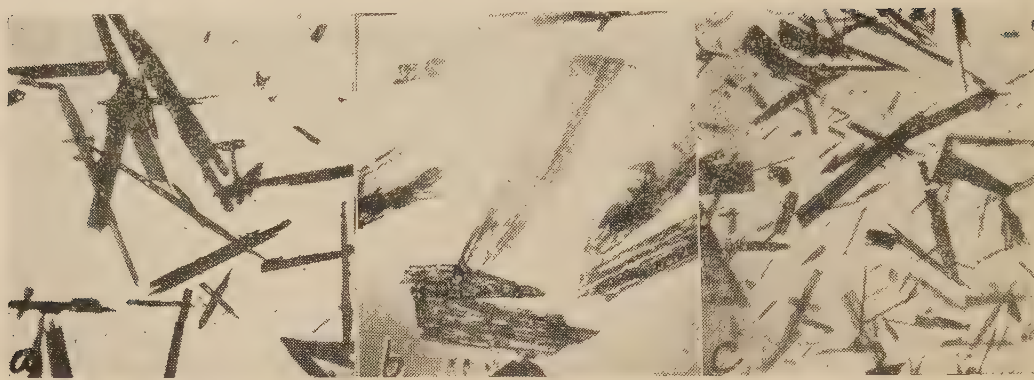


Fig. 1

(a) Crystals of Adenine-monopicrat; Magnification 80× ; m. p. 281°C

(b) Crystals of Histidine-dipicrat; Magnification 21.6× ; m. p. 86°C

(c) Crystals of Lysine-monopicrat; Magnification 80× ; m. p. 251°C

考　　察

ウツプルイノリ500gの熱湯抽出エキスの全窒素量は6.82gにして全窒素量の23.8%に相當し、この中49.2%即ち3.36gが非蛋白窒素である。これを100%とせる時、塩基性部全窒素量は21.9%であつた。而して塩基性部窒素の分布は 1) プリン塩基の部……49.3%、2) ヒスチヂン塩基の部……8.[illegible]%、3) アルギニン塩基の部……6.3%、4) リジン塩基の部……35.3%にしてプリン塩基區分が最も多く、次はリジン塩基區分にしてヘキソン塩基區分は最も少かつた。而してヘキソン塩基區分中ヒスチヂンの含量が多い事を認めた。これは荻野氏が *Sargassum Ringgoldianum* について認めた結果と同樣である。戸田氏は *Porphyra umbilicalis* 中のリジン塩基區分よりスタキドリンを分離確認しているが、本研究に於ては試料僅少のためそれを捕取することが出來なかつた。又昇汞による沈澱物を充分精査することが出來なかつたが恐らくコリンの存在も容易に想定される所である。又アルギニン塩基の部よりアルギニンをフラビアネートとして分離確認する事は出來なかつたがこれは實驗操作の悪かつたゝめと思われる。

要　　約

ウツプルイノリ (*Porphyra pseudolinearis*) 中に遊離に存在している塩基性物質についてその系統的分離を試み、その結果として

(1) アデニン、ヒスチヂン及びリジンをピクレートとして分離した。尚アルギニン、コリンも存在するものと思われる。

(2) ウツプルイノリの窒素分布狀態の大體の狀況を明らかにした。

終りに臨み終始御懇切な御指導と御鞭撻とを賜わりし本學部教授農學博士、醫學博士村田喜一先生に深甚なる謝意を表する次第である。

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（水產科學研究所業績　第97號）

太陽觀測による正午位置決定に就て

平岩　節　(航海運用學教室)

ON THE DETERMINATION OF NOON POSITION BY THE OBSERVATION OF THE SUN

Takashi HIRAIWA

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In the case of the determination of noon position by both ante-meridian and noon sights by the sun, it is generally considered to be best that 1st sight should be made about 8a.m., or when its azimuth is near 90°.

However, the former is based upon customary practice, while the latter deals with both of two position lines equally precise, without considering the error due to transferring the position line. Hence, each of them is not theoretical.

In this paper, the writer treated of the probable best opportunities to observe 1st sight according to various combinations of latitude and declination.

Table 1 shows the values of the best opportunities to observe 1st sights.

Fig. 2 shows respectively, the reliability of ship positions obtained by both observations at the best opportunities to observe 1st sights and at noon, by which it can be confirmed that the case when latitude and declination are of the same sign is better than when they are of contrary signs.

Fig. 3 shows the azimuths of the sun at the best opportunities to observe 1st sights, which generally lie between 50° and 70°; accordingly it cannot easily be said that it is preferable to observe 1st sight when its azimuth is near 90°.

In this paper, the writer dealt with a standard error of each observation as 0′.74, and an error of estimated position as $0'.74\sqrt{t}$ (t: hour), which under various circumstances are not free from some differences. Accordingly some discrepancies can scarcely be avoided in comparison with the values of the table 1.

However, the writer hopes herewith that it may become a useful guide to learning the best opportunity to observe 1st sight by the sun.

1. 緒　　言

天體觀測により正午位置を決定する方法として一般船舶にありては太陽の午前觀測と子午線高度觀測による位置の線の組合せによつてゐる。つまり二本の位置の線の交點を以て決定船位とするのである。

二本の位置の線による船位の確率密度は位置の線が直交するとき最大であるから最良の組合せであるが、これは飽く迄等精度の場合に就て言えるのであつて航行船舶に於ける如く轉位の線による場合

にありては赤緯と緯度との組合せに應じて最良の交角は變化するものである。從つて交角が直角に近い方がよいとか習慣的に午前8時に觀測すればよいとか言うのは余りにも粗雜な言であるといわねばなるまい。

最近船位誤差に確率的解明が施されつゝあるは寔に喜ぶべき現象である。本文に於ては一般に行われてゐる太陽の午前觀測と正午觀測による正午位置決定法に於て各緯度、赤緯に應じて如何なる時角のとき觀測を行えばよいか、換言すれば午前觀測の最良の時機に就て述べる。尙本文に於て使用せる單觀測の誤差量は海務院鮫島教授等の行える觀測結果に依つたものであり記して同氏等に謝意を表する。

2. 二本の位置の線の交點の確率密度

Fig.1 に於て第一觀測時の推定船位を A, 正午の推定位置を B とすれば正午位置は兩位置の線の交點 O として決定される。今二本の位置の線を X, Y; その交角を φ とし、X, Y の誤差が何れも正規分布に從うものとし X, Y の標準誤差（即ち實測値の標準偏差）を夫々 σ_1, σ_2 とすれば $\sigma y=\frac{\sigma_1}{\sin\varphi}$, $\sigma x=\frac{\sigma_2}{\sin\varphi}$

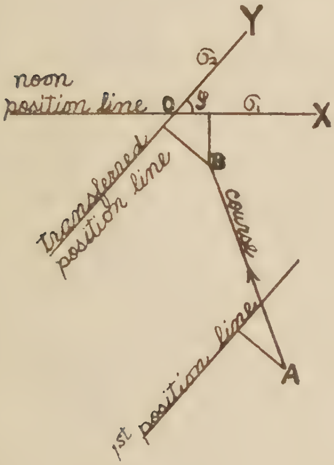


Fig.1

Y の確率密度函數は

$$f_2(y)=\frac{\sin\varphi}{\sqrt{2\pi}\,\sigma_1}\,e^{-\sin^2\varphi\frac{y^2}{2\sigma_1^2}}$$

X の確率密度函數は

$$f_1(x)=\frac{\sin\varphi}{\sqrt{2\pi}\,\sigma_2}\,e^{-\sin^2\varphi\frac{x^2}{2\sigma_2^2}}$$

故に眞位置の横座標が x と x+dx との間、縦座標が y とy+dy との間の平行四邊形の中に落ちる確率は

$$\frac{\sin\varphi}{2\pi\,\sigma_1\,\sigma_2}\,e^{-\sin^2\varphi\left(\frac{x^2}{2\sigma_2^2}+\frac{y^2}{2\sigma_1^2}\right)}\sin\varphi.\ dx.\ dy.$$ となる。

こゝに dx. dy. $\sin\varphi$ はこの平行四邊形の面積であるから $\frac{\sin\varphi}{2\pi\,\sigma_1\,\sigma_2}\,e^{-\sin^2\varphi\left(\frac{x^2}{2\sigma_2^2}+\frac{y^2}{2\sigma_1^2}\right)}$ は同時分布の確率密度函數である。故に交點 O の確率密度 (k) は上記の probability density function に於て x=0, y=0 とおけば $k=\frac{\sin\varphi}{2\pi\,\sigma_1\sigma_2}$ である。

3. 午前觀測の最適機

$k=\frac{\sin\varphi}{2\pi\,\sigma_1\,\sigma_2}$ に於て $\sigma_1=\sigma_2$ なるときは $\varphi=90°$ のとき即ち位置の線が直交するとき k は最大であることは容易に言える。換言すれば位置の線の精度が等しいとき二回の觀測により觀測位置を決定するには方位の差が 90° なるときが最もよいということである。航行船舶にありては同時觀測によらなければ $\sigma_1=\sigma_2$ ということは考えられない。本文で採上げてゐる隔時觀測の場合にありては勿論 $\sigma_1\neq\sigma_2$ である故 $\frac{\sin\varphi}{\sigma_1\sigma_2}$ を最大ならしめることを考えねばならない。こゝに單觀測の標準誤差 $\sigma_1=$

0.′74. 又推定位置の標準誤差は海潮流、皮流による一時間當りの標準誤差を 0.′6、操舵の標準誤差を 1.°3、自差の不正確に基づくものを0.°6、推定風壓差によるものを1.°3、測程儀示度の標準誤差を2%と假定すれば、數時間内に於ける前後左右の標準誤差は共に近似的に $0.'74\sqrt{t}$ にて表わされる（但し t は航走時間）。從つて $\sigma_2=0.'74\sqrt{1+t}$ 依つて $k=\frac{\sin\varphi}{2\pi(0.74)^2\sqrt{1+t}}$ ………… (1) を最大ならしむればよいことになる。

太陽の隔時觀測による正午位置決定の場合に於ては (1) 式は次の様にかきかえることが出來る。

$$k=c\frac{\sin Z}{\sqrt{1+h}}$$

c………常　數

Z………1^{st} Sight に於ける太陽の方位

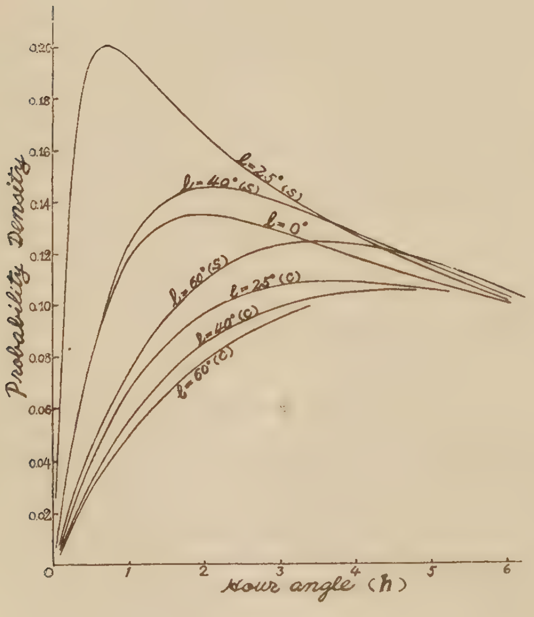
h………1^{st} Sight に於ける太陽の時角（時）

これを最大ならしめる條件は h が小で Z が大であればよいが h と Z との間には之に相反する性質があり又 Sin Z を h にて置き換えて極大値を求めるのは解法上困難である。それ故筆者は h の最大値附近に於ける刻々の h に對する Z を求め k の最大となる h を得る方法をとつた。第 1 表はその結果を示す。こゝに實際問題として上述の觀測値及び推定位置の標準誤差は過去の經驗、觀測結果等よりの知識から大體の値が知れてゐるにすぎない關係上數値に左程精密な數字を必要としないし、又確率密度も短時間内に於ては急增減はないので赤緯は 5° 間隔とし、緯度は表使用上便利な様に 1° 間隔とした。表の使用に當つて赤緯の中間値に對しては目算によつて結構である。又その時の緯度、赤緯の大きさに應じて時角に幅をもたせて差支ない。尚表中※印を附せるものより高緯度のものは最適機の計算値が日出前になるからかゝる場合には日出後適當な高度に達するのを待つて觀測すればよい。

一例として赤緯が 20°、緯度が 0°, 25°, 40° 60° の場合を考えれば最適機の時角は夫々 $1^h 56^m$, 41^m(Same sign) $3^h 56^m$(Contrary sign), $2^h 6^m$(S) $4^h 44^m$(C), $3^h 34^m$(S) $5^h 11^m$(C), $3^h 24^m$(Sun rise), となるが k 値の變化の狀態を graph に畫いて見た。

Fig. 2 が即ちそれである。同圖を通して最適機として許容さるべき時角の幅がよく判ると思う。

Fig. 2. Probability densities of the intersecting points according to each hour angle when declination is 20°; latitude 0°, 25°, 40°, 60°.
Here { S…same sign (l. d)
　　　C…contrary sign (l. d)



4.　最適機の比較及び方法

3. に述べた如く赤緯と緯度とが與えられゝばそれに對する天測最適機は求められるが、それ等の最適機に觀測した場合決定船位の確らしさは k の値によつて勿論異る。つまり k が大きくなれば船位の確らしさは

Table. 1. Best hour angle to observe 1 st sight

l \ d	l. d; Same sign 0°	5°	10°	15°	20°	23°	l. d; Contrary sign 0°	5°	10°	15°	20°	23°
0°	—	38^{m}	$1^{h}\ 8^{m}$	$1^{h}\ 32^{m}$	$1^{h}\ 56^{m}$	$2^{h}\ 10^{m}$	—	38^{m}	$1^{h}\ 8^{m}$	$1^{h}\ 32^{m}$	$1^{h}\ 56^{m}$	$2^{h}\ 10^{m}$
1	12^{m}	33	1 3	1 27	1 51	2 6	12^{m}	44	1 13	1 37	2 1	2 15
2	20	27	57	1 23	1 47	2 2	20	50	1 18	1 42	2 5	2 19
3	27	21	51	1 18	1 42	1 57	27	56	1 22	1 47	2 10	2 24
4	33	13	45	1 13	1 38	1 53	33	$1^{h}\ 2^{m}$	1 27	1 52	2 14	2 28
5	39	—	40	1 8	1 33	1 48	39	1 7	1 32	1 56	2 19	2 32
6	44	12	34	1 3	1 28	1 44	44	1 12	1 37	2 1	2 23	2 37
7	50	20	27	58	1 23	1 39	50	1 17	1 42	2 6	2 28	2 41
8	55	26	21	52	1 18	1 34	55	1 22	1 46	2 10	2 32	2 46
9	$1^{h}\ 1^{m}$	33	13	47	1 13	1 29	$1^{h}\ 1^{m}$	1 27	1 50	2 14	2 36	2 50
10	1 6	38	—	41	1 8	1 24	1 6	1 32	1 55	2 19	2 41	2 54
11	1 12	44	10	34	1 3	1 19	1 12	1 37	1 59	2 23	2 45	2 59
12	1 17	50	18	28	58	1 14	1 17	1 42	2 4	2 27	2 49	3 3
13	1 22	55	25	20	53	1 9	1 22	1 46	2 9	2 32	2 54	3 8
14	1 27	$1^{h}\ 1^{m}$	32	11	48	1 4	1 27	1 51	2 13	2 37	2 58	3 12
15	1 32	1 6	39	—	42	59	1 32	1 56	2 18	2 41	3 2	3 16
16	1 37	1 11	45	10	36	54	1 37	2 1	2 22	2 45	3 8	3 21
17	1 42	1 16	51	20	30	48	1 42	2 5	2 27	2 50	3 11	3 25
18	1 47	1 22	57	28	22	43	1 47	2 10	2 31	2 54	3 15	3 30
19	1 52	1 27	$1^{h}\ 2^{m}$	35	13	36	1 52	2 15	2 36	2 59	3 20	3 34
20	1 56	1 32	1 8	42	—	30	1 56	2 19	2 40	3 3	3 24	3 39
21	2 1	1 37	1 13	48	12	23	2 1	2 24	2 45	3 8	3 28	3 43
22	2 6	1 43	1 19	54	22	14	2 6	2 28	2 49	3 12	3 33	3 48
23	2 11	1 48	1 24	59	29	—	2 11	2 33	2 54	3 16	3 37	3 52
24	2 15	1 53	1 30	$1^{h}\ 5^{m}$	35	13	2 15	2 37	2 58	3 21	3 42	3 56
25	2 20	1 58	1 35	1 10	41	22	2 20	2 42	3 3	3 25	3 46	4 1
26	2 25	2 3	1 40	1 15	48	30	2 25	2 46	3 7	3 29	3 50	4 5
27	2 29	2 8	1 45	1 21	54	36	2 29	2 51	3 12	3 33	3 55	4 9
28	2 34	2 12	1 50	1 26	59	42	2 34	2 55	3 16	3 38	3 59	4 13
29	2 39	2 17	1 55	1 31	$1^{h}\ 5^{m}$	48	2 39	3 0	3 20	3 42	4 3	4 17
30	2 43	2 22	2 0	1 36	1 11	55	2 43	3 4	3 25	3 46	4 7	4 21
31	2 47	2 26	2 5	1 41	1 17	$1^{h}\ 1^{m}$	2 47	3 8	3 29	3 50	4 11	4 25
32	2 52	2 31	2 10	1 47	1 22	1 7	2 52	3 12	3 33	3 54	4 15	4 30
33	2 56	2 35	2 15	1 52	1 28	1 13	2 56	3 16	3 37	3 58	4 19	4 34
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38	3 16	2 57	2 37	2 17	1 55	1 41	3 16	3 36	3 58	4 17	4 38	4 52
39	3 20	3 1	2 42	2 21	2 0	1 46	3 20	3 40	4 1	4 20	4 41	4 55
40	3 24	3 5	2 46	2 26	2 6	1 52	3 24	3 44	4 5	4 23	4 44	4 58
41	3 28	3 9	2 50	2 30	2 11	1 57	3 28	3 47	4 8	4 26	※4 48	5 1
42	3 32	3 13	2 55	2 35	2 16	2 2	3 32	3 51	4 12	4 29	4 50	5 3
43	3 35	3 18	2 59	2 40	2 21	2 8	3 35	3 54	4 15	4 32	4 53	5 5
44	3 39	3 21	3 3	2 44	2 26	2 13	3 39	3 57	4 18	4 35	4 55	5 7
45	3 42	3 25	3 7	2 49	2 31	2 18	3 42	4 0	4 20	4 38	4 57	5 9
46	3 46	3 29	3 11	2 53	2 35	2 23	3 46	4 3	4 22	4 40	4 59	5 10
47	3 49	3 32	3 15	2 57	2 40	2 28	3 49	4 6	4 25	4 43	5 1	5 12
48	3 52	3 36	3 19	3 2	2 45	2 33	3 52	4 9	4 27	4 45	5 2	5 13
49	3 55	3 39	3 23	3 6	2 49	2 37	3 55	4 12	4 29	4 47	5 4	5 15
50	3 58	3 42	8 26	3 10	2 54	2 42	3 58	4 15	4 31	※4 49	5 5	5 16
51	4 1	3 46	3 30	3 14	2 58	2 46	4 1	4 17	4 33	4 51	5 6	5 17
52	4 4	3 49	3 34	3 18	3 2	2 51	4 4	4 19	4 35	4 52	5 7	5 18
53	4 7	3 52	3 37	3 22	3 6	2 55	4 7	4 21	4 37	4 53	5 8	5 19
54	4 9	3 55	3 41	3 26	3 10	3 0	4 9	4 23	4 39	4 54	5 9	5 19
55	4 12	3 58	3 44	3 30	3 14	3 4	4 12	4 25	4 41	4 55	5 10	5 20
56	4 14	4 1	3 48	3 33	3 18	3 8	4 14	4 27	4 42	4 56	5 10	5 20
57	4 17	4 3	3 51	3 37	3 22	3 13	4 17	4 29	4 43	4 57	5 10	5 20
58	4 19	4 6	3 53	3 40	3 26	3 17	4 19	4 31	4 44	4 58	5 10	5 20
59	4 21	4 8	3 56	3 43	3 30	3 21	4 21	4 32	4 45	4 59	5 11	5 20
60	4 22	4 10	3 58	3 46	3 34	3 25	4 22	4 33	4 46	4 59	5 11	5 20

Fig. 3. Probability density of the intersecting point of the two position lines gotten from 1st sight at the best time and noon sight.
The sign ······ shows the probability density in the combination of sunrise and noon.

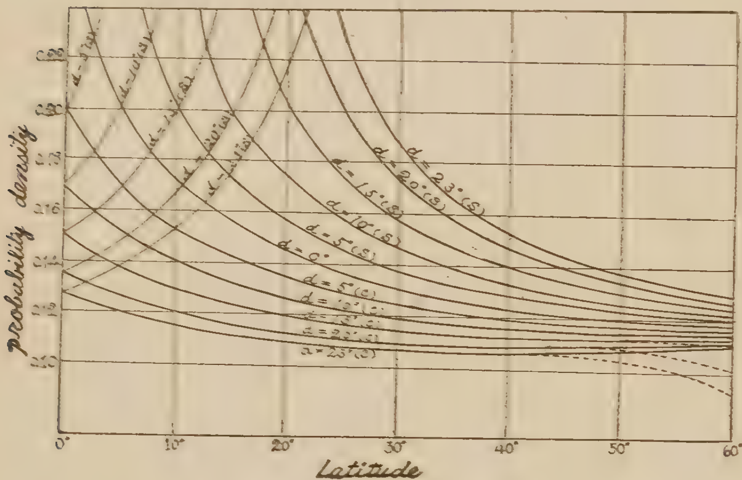
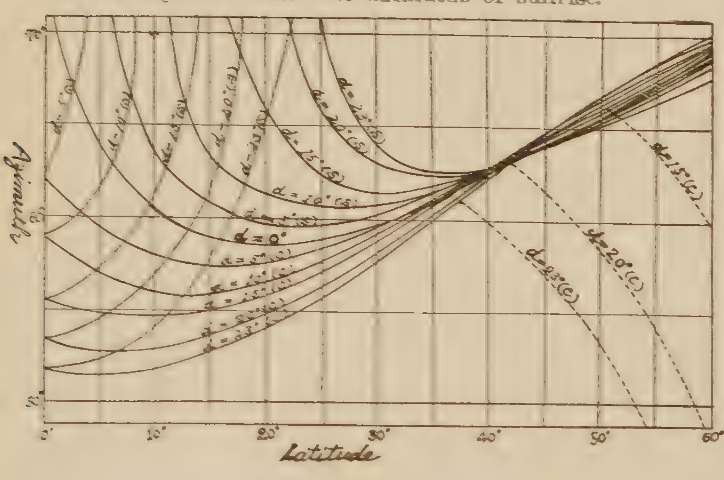


Fig. 4. Azimuth of the sun at the best time to observe 1st sight.
The sign ······ shows the azimuths of sunrise.



增す。換言すれば誤差界は當然小となるので行船上は k の値を可及的大ならしめたいのであるが k の最大値は前述の如く緯度、赤緯によつて決定されるもので如何とも出來ない。然し乍ら與えられた條件下に於て最良の時機を見出すことは航海上必要なること論を俟たない。Fig. 3 は各緯度、赤緯に對する最適機觀測と正午觀測より得たる二本の位置の線の交點の確率密度を畫いたもので赤緯と緯度とが異符號のときより同符號の時の方が良好であることが判る。

又 Fig 4 は最適機に於ける太陽の方位を示す。

同圖に見る如く最適機の方位は大體 50° から 70° の間に位するもので漫然と 90° に近い方がよいと言うことは出來ない。

5. 結　　　言

船位の確からしさは位置の線の數が多ければ多い程大となることは既に知られてゐるところである。その點から言えば午前と正午の二回の觀測では條件が悪いと言える。これは一つには日中太陽以外の天體觀測の機會に恵まれないという悪い條件によつてゐるので已むを得ないところである。又船位決定の點から見れば、他に方法は考えられるが從來の習慣として正午位置に重點をおいてゐる關係上從來の午前と正午觀測の組合せの吟味、検討を行つた。

尚本文中單觀測の標準誤差を 0.7' として扱つたがこの値は觀測者個々に就て異ること勿論であ

る。而も確率密度は單觀測の標準誤差に左右されるものであるから觀測技術の向上が望まれる。それと他の一つは本文に述べたるは推定船位の標準誤差を 0.′74 $\sqrt{t}$ として取扱つているので個々の場合若干の相違あるは免れない。從つて最適機に幾らかのずれの生ずるのは不可避であるが、天測時機の基準となれば幸甚である。又決定船位に就て適當な誤差界を考え航海の萬全を期すること航海者として一層大切な事であると思う。

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